Evaporation of the ether–pentane eluate and distillation of the residue gave 1.4 g. (6.5%) of 2-ethyl-4-methoxy-6-phenyl-*s*-triazine, b.p. 100–103° (0.1 mm.), $n^{31}\text{D}$ 1.5700, which crystallized on standing in needles: m.p. 28.5–30.5°; $\lambda_{\max}$ 263 mμ (ϵ 20,500); and infrared absorption, 1545 (triazine ring), 1350, 1095, 1055, 928, and 839 (common to 2,4-diethyl-6-methoxy-*s*-triazine[10]) and 781, 730, and 687 cm.$^{-1}$ (phenyl ring).

Anal. Calcd. for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.53; O, 7.42. Found: C, 66.59; H, 5.94; N, 19.65; O, 7.57.

2 Ethyl 4-methyl-6-phenyl-*s*-triazine (VIg).—Reaction of 19.1 g. of methyl N-propionylbenzimidate with acetamidine (from 10.4 g., 0.11 mole, of hydrochloride) was performed in a manner exactly similar to that of the previous experiment and was followed by a similar work-up. The pentane extract was adsorbed on 150 g. of alumina and eluted with 4500 ml. of pentane. Distillation of the residue after removal of pentane gave 10.0 g. of oil, b.p. 88° (0.1 mm.), which was shown by g.l.c. analysis to contain 9.42 g. (by calculation, 47.6% yield) of 2-ethyl-4-methyl-6-phenyl-*s*-triazine, 0.41 g. (1.9%) of 2,4-diethyl-6-phenyl-*s*-triazine, and 0.16 g. (1.2%) of methyl benzoate. The middle cut of the distillation, $n^{30}\text{D}$ 1.5700, 97% content of the main product, was used for analysis: $\lambda_{\max}$ 263 mμ (ϵ 21,500); and infrared absorption, 1540 (triazine ring), 930, 867, 797, 752, and 695 cm.$^{-1}$ (phenyl ring).

Anal. Calcd. for $C_{12}H_{13}N_3$: C, 72.33; H, 6.57; N, 21.09. Found: C, 72.33; H, 6.58; N, 20.80.

Acknowledgment.—The author wishes to express his thanks to Mr. C. G. Santangelo for technical assistance, to Mr. John J. Kobliska and his staff for the microanalyses, and to Mr. A. M. Ferri for the ultraviolet spectra.

Syntheses and Reactions of 5-Alkyl-4-amino-3-hydrazino-*s*-triazoles

H. H. TAKIMOTO, G. C. DENAULT, AND S. HOTTA

Chemical Propulsion Department, Laboratories Division, Aerospace Corporation, El Segundo, California

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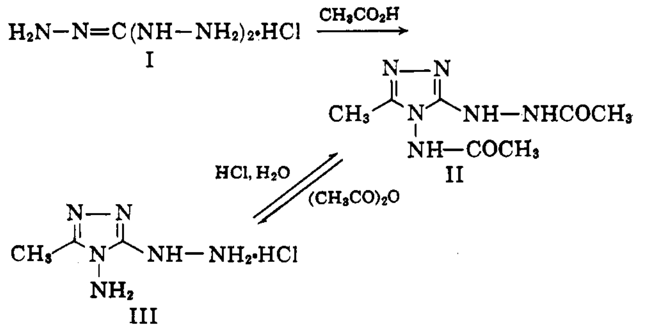
Triaminoguanidine hydrochloride was treated with acetic and propionic acids to yield 5-alkyl-4-amino-3-hydrazino-*s*-triazole hydrochlorides. An organic azide was prepared from the triazole and thermally decomposed after treatment with benzaldehyde to yield 1H-3-methyl-2-phenyl-*s*-triazolo[3,2-*c*]-*s*-triazole. Other reactions of the triazoles with benzaldehyde, acetic anhydride, and 2,4-pentanedione are described.

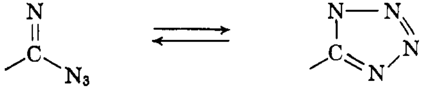
Although a number of methods are available for the preparation of *s*-triazoles, few are amenable for the synthesis of 4H-3-hydrazino-*s*-triazole derivatives. These compounds have been obtained by the reduction of nitroaminotriazoles,[1] the hydrolysis of semicarbazidotriazole,[2] and the reaction of N,N′-dithiocarbamylhydrazine[3] with hydrazine. Alternatively, triaminoguanidine hydrochloride (I) has been reported[4] to react with formic acid to yield a *s*-triazole derivative, whereas, I with acetic acid yielded only a resinous product. We have reinvestigated the reaction of triaminoguanidine hydrochloride with acetic acid and with propionic acid and have obtained the 5-alkyl-4-amino-3-hydrazino-*s*-triazole hydrochlorides in good yield. The syntheses and reactions of these triazoles are described in this report.

As reported by earlier workers,[4] refluxing I in acetic acid and removal of the solvent produced a viscous, resinous residue. From this residue, a moderate yield of 4-acetamido-3-acethydrazino-5-methyl-*s*-triazole hydrochloride (II) was isolated when extreme care was taken to remove the last traces of volatiles. However, when the viscous residue was refluxed in dilute hydrochloric acid, an excellent yield of 4-amino-3-hydrazino-5-methyl-*s*-triazole hydrochloride (III) was obtained. The difficulties encountered in the isolation of the diacetyl derivative II were presumably due to the formation of a mixture of triazoles acetylated to varying extents, which upon acid hydrolysis yielded a crystalline hydrochloride.



The present study was extended to propionic and benzoic acid. Although the latter acid failed to yield the cyclized product, propionic acid readily gave 4-amino-5-ethyl-3-hydrazino-*s*-triazole hydrochloride (IV) following the procedure for acetic acid. The 4-benzylidenehydrazino derivative was obtained by the reaction of IV with benzaldehyde.

The 3-hydrazino group of the triazole III was converted to an azido group by treatment with one equivalent of nitrous acid. Subsequent reaction of this azido compound with benzaldehyde yielded 3-azido-4-benzylideneamino-5-methyl-*s*-triazole (V). Although the azido group attached to the carbon atom of the azomethine linkage can readily undergo ring closure to form a tetrazole, the infrared spectrum of V taken on a potassium bromide wafer exhibited an intense band at 2150 cm.$^{-1}$ characteristic of azides.[5]



Compound V, when heated in chlorobenzene, smoothly liberated 1 mole of nitrogen. The azene (univalent, uncharged nitrogen) intermediate[6] thus

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(1) (a) W. Manchot and R. Noll, *Ann.*, **343**, 1 (1905); (b) W. Manchot, *Ber.*, **43**, 1312 (1910); (c) R. A. Henry, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, **75**, 955 (1953); (d) E. Lieber, S. Schiff, R. A. Henry, and W. Finnegan, *J. Org. Chem.*, **18**, 218 (1953).

(2) H. Gehlen and F. Lemme, *Naturwissenschaften*, **50**, 645 (1963).

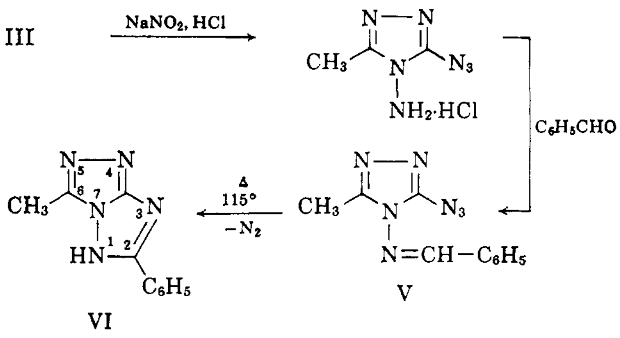
(3) E. Hoggarth, *J. Chem. Soc.*, 4817 (1952).

(4) C. F. Kröger, G. Etzold, and H. Beyer, *Ann.*, **664**, 146 (1963).

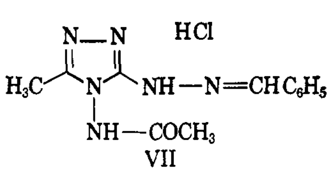
(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 15.

(6) For a review of univalent, uncharged nitrogens, see R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

formed underwent an intramolecular cyclization at the azomethine linkage to form 1H-6-methyl-2-phenyl-*s*-triazolo[3,2-*c*]-*s*-triazole (VI). This product, which exhibited a single maxima in ethanol at 248 mμ (ε 20,800) in the ultraviolet, has been prepared[7] previously from 3,4-diamino-5-methyl-*s*-triazole and benzoyl chloride. The attack of the azene at the azomethine linkage is analogous to the thermolytic decompositions of 2-azidobenzylideneamines[8] and benzylidene-2-azidoanilines.[9] A detailed study of the decompositions of 3-azido-4-benzylideneamino-*s*-triazole derivatives will be described in a later report.

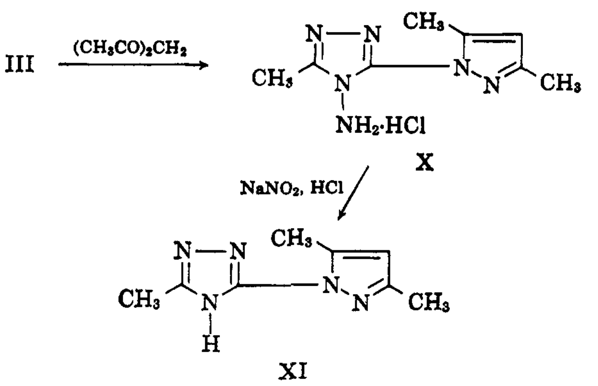


The hydrolysis of the diacetyl compound II in water followed by treatment with benzaldehyde yielded a triazole derivative containing a monoacetyl and monobenzylidene group. The resulting product may be either the 4-acetamido-3-benzylidenehydrazino- or the 3-acethydrazino-4-benzylideneamino-*s*-triazole hydrochloride. Although the hydrolysis would be expected to occur first at the 3-acethydrazino position, the facile rearrangement of the substituent from 4- to the 3-position in 4-amino-3-hydrazino-*s*-triazole has been reported.[4] Thus, it is possible that the expected 4-acetamido, initially formed, would rearrange to the 3-acethydrazino and then react with benzaldehyde. The structure of the above product was established as 4-acetamido-3-benzylidenehydrazino-5-methyl-*s*-triazole hydrochloride (VII) by the stepwise preparation of this compound. The reaction of III with benzaldehyde yielded 4-amino-3-benzylidene-5-methyl-*s*-triazole hydrochloride (VIII) and subsequent acetylation of the 4-amino group produced VII. Furthermore, VIII was converted to the dibenzylidene derivative by reaction with a second mole of benzaldehyde.



VII

In analogy with the work of Beyer,[4] *et al.*, III was treated with 2,4-pentanedione resulting in a condensation and cyclization to produce 1-(4-amino-5-methyl-*s*-triazol-3-yl)-3,5-dimethylpyrazole hydrochloride (X). This compound was readily deaminated by treatment with nitrous acid to yield XI and also converted to the N-benzylidene derivative XII upon reaction with benzaldehyde.



Experimental[10,11]

Triaminoguanidine Hydrochloride (I).—The procedure[12] described for the preparation of triaminoguanidine nitrate was used. Hydrazine (15 ml.) was added to 9.5 g. of guanidine hydrochloride in 50 ml. of distilled water. The pink-colored solution was set aside in an open dish with a periodic addition of hydrazine. The solid (11.6 g.) which had separated was collected after 5 days. The product was recrystallized from methanol yielding white needles melting at 237–239° dec. (lit.[13] m.p. 234–236°).

4-Acetamido-3-acethydrazino-5-methyl-*s*-triazole Hydrochloride (II).—A green solution of 8.42 g. of I in 50 ml. of acetic acid was refluxed for 6 hr. The volatiles were removed under vacuum leaving an extremely viscous, greenish white residue. The complete removal of the last traces of volatiles appeared to facilitate the isolation procedure. The crude product was triturated with ethanol yielding 8.7 g. (59.4%) of a white solid melting at 227–231° dec. An analytical sample, m.p. 239–244°, dec., was obtained by recrystallizations from acetic acid.

Anal. Calcd. for $C_7H_{13}ClN_6O_2$: C, 33.80; H, 5.27; Cl, 14.26; N, 33.80. Found: C, 33.85; H, 5.38; Cl, 14.07; N, 33.72.

The above product was also obtained by refluxing a solution of 4-amino-3-hydrazino-5-methyl-*s*-triazole hydrochloride (III) with 2 equiv. of acetic anhydride in acetic acid.

4-Amino-3-hydrazino-5-methyl-*s*-triazole Hydrochloride (III).—A solution of 10.0 g. of I in 50 ml. of acetic acid was refluxed for 16 hr. The color of the solution varied from green to blue depending on the purity of the starting material. The acetic acid was removed under partial vacuum leaving a frothy, bluish white residue. This residue was dissolved in 100 ml. of 6 *N* hydrochloric acid and the blue solution turned light brown during the refluxing period of 2 hr. Upon removal of the volatiles, a white crystalline solid was obtained. This solid was triturated with hot ethanol to yield 12.0 g. (93.8%) of product melting at 235–245° dec. An analytical sample, m.p. 248–250° dec., was obtained by recrystallizations from ethanol.

Anal. Calcd. for $C_3H_9ClN_6$: C, 21.89; H, 5.51; N, 51.06. Found: C, 22.01; H, 5.78; N, 51.20.

4-Amino-5-ethyl-3-hydrazino-*s*-triazole Hydrochloride (IV).—This compound was prepared using propionic acid in 89.6% yield according to the procedure described above for III. Recrystallizations from ethanol yielded an analytical sample, m.p. 232–234° dec.

Anal. Calcd. for $C_4H_{11}ClN_6$: C, 26.90; H, 6.20; N, 47.05. Found: C, 27.0; H, 6.25; N, 47.3.

The treatment of IV with benzaldehyde produced 4-amino-3-benzylidenehydrazino-5-ethyl-*s*-triazole hydrochloride in 93.5% yield. An analytical sample, m.p. 236–238° dec., was obtained by recrystallizations from ethanol.

Anal. Calcd. for $C_{10}H_{15}ClN_6$: C, 49.54; H, 5.67; N, 31.51. Found: C, 49.3; H, 5.90; N, 31.7.

3-Azido-4-benzylideneamino-5-methyl-*s*-triazole (V).—A solution of 1.38 g. of sodium nitrite in 10 ml. of water was added dropwise to a cold solution (ice–salt bath) of 3.29 g. of III in 20 ml. of

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(7) H. Gehlen and G. Röbisch, *Ber.*, **660**, 148 (1962).

(8) L. Krbechek and H. Takimoto, *J. Org. Chem.*, **29**, 1150 (1964).

(9) L. Krbechek and H. Takimoto, *ibid.*, **29**, 3630 (1964).

(10) All melting points are uncorrected.

(11) Analyses were performed by Micro-Tech Laboratories, Skokie, Ill., and in this laboratory.

(12) T. E. O'Connor, K. Horgan, and J. Reilly, *J. Appl. Chem.*, **1**, 91 (1951).

(13) D. W. Kaiser and G. A. Peters, U. S. Patent 2,721,218 (Oct. 18, 1955); *Chem. Abstr.*, **50**, 8718 (1956).

water and 10 ml. of 2 *N* hydrochloric acid. The solution was stirred in the cold for 30 min. and then 1.06 g. of benzaldehyde was added. After 10 min. stirring at room temperature, solid began to appear in the mixture. The beige-colored solid was separated after 2 hr. yielding 2.15 g. (47.3%) of product melting at 107–111° with considerable bubbling. The product was purified by dissolving in cold ethanol and precipitating by the addition of water to yield a straw-colored solid, m.p. 109–111° dec.

Anal. Calcd. for $C_{10}H_9N_7$: C, 52.85; H, 4.00; N, 43.16. Found: C, 52.80; H, 4.18; N, 43.10.

Decomposition of 3-Azido-4-benzylideneamino-5-methyl-*s*-triazole (V).—A solution of 2.27 g. of V in 250 ml. of chlorobenzene was decomposed by heating at 115–120°. A smooth liberation of gas was observed at this temperature, although some bubbling was initially observed at about 100°. A total of 217 ml. (theory 224 ml.) was collected during the first 2 hr.; however, heating was continued for 4 hr. Upon cooling to room temperature, a white solid separated from the bright yellow reaction mixture. This solid was collected by filtration and the filtrate was concentrated to yield additional solid. A total of 1.78 g. (89.6%) of the 1H-6-methyl-2-phenyl-*s*-triazolo[3,2-*c*]-*s*-triazole (VI) melting at 223–226° was obtained. Recrystallizations from benzene containing a small amount of alcohol yielded white needles, m.p. 226–228° (lit.[7] m.p. 228.5°).

Anal. Calcd. for $C_{10}H_9N_5$: C, 60.29; H, 4.56; N, 35.16. Found: C, 60.57; H, 4.63; N, 35.29.

4-Acetamido-3-benzylidenehydrazino-5-methyl-*s*-triazole Hydrochloride (VII). A.—Benzaldehyde (1.1 g.) was added to a solution of 2.48 g. of the diacetyl derivative II in 30 ml. of water, 2 ml. of ethanol, and 1 drop of concentrated hydrochloric acid. The yellow solution was heated gently at 60–80° for 30 min. when a voluminous quantity of white precipitate separated. The mixture was cooled to room temperature and the solid was collected by filtration to yield 1.75 g. (59.3%) of product melting at 275–283° dec. This product was recrystallized from ethanol containing a few drops of 6 *N* hydrochloric acid to yield an analytical sample, m.p. 302–304° dec.

Anal. Calcd. for $C_{12}H_{15}ClN_6O$: C, 48.89; H, 5.13; Cl, 12.03; N, 28.52. Found: C, 48.98; H, 5.32; Cl, 12.01; N, 28.5.

B.—A solution of 2.53 g. of 3-benzylidenehydrazino-4-amino-5-methyl-*s*-triazole hydrochloride (VIII) and 1.10 g. of acetic anhydride in 60 ml. of acetic acid was heated for 15 min. The white solid which separated was collected by filtration yielding 1.60 g. (54.3%) of product melting at 270–280° dec. The product was recrystallized from ethanol, m.p. 302–304° dec. A mixture melting point with 4-acetamido-3-benzylidenehydrazino-5-methyl-*s*-triazole hydrochloride (VII) prepared earlier showed no depression. Furthermore, their infrared spectra were identical.

4-Amino-3-benzylidenehydrazino-5-methyl-*s*-triazole Hydrochloride (VIII).—This compound was prepared from III and benzaldehyde in 83% yield. An analytical sample, m.p. 250–251° dec., was obtained by recrystallizations from ethanol.

Anal. Calcd. for $C_{10}H_{13}ClN_6$: C, 47.52; H, 5.19; N, 33.26. Found: C, 47.4; H, 5.12; N, 33.4.

4-Benzylideneamino-3-benzylidenehydrazino-5-methyl-*s*-triazole (IX).—This compound was prepared in 75.6% yield by the reaction of III with excess benzaldehyde and triethylamine. A bright yellow analytical sample, m.p. 187.5–189°, was obtained by recrystallizations from benzene.

Anal. Calcd. for $C_{17}H_{16}N_6$: C, 67.09; H, 5.30; N, 27.62. Found: C, 66.99; H, 5.21; N, 27.5.

1-(4-Amino-5-methyl-*s*-triazol-3-yl)-3,5-dimethylpyrazole Hydrochloride (X).—A solution of 1.65 g. of III and 1.00 g. of 2,4-pentanedione in 75 ml. of ethanol was refluxed for 1 hr. The solvent was removed leaving a pale yellow residue (2.14 g., 93.5%) melting at 183–192°. A white solid melting at 192–195° was obtained by recrystallizations from isopropyl alcohol containing a few drops of 6 *N* hydrochloric acid.

Anal. Calcd. for $C_8H_{13}ClN_6$: C, 42.02; H, 5.73; N, 36.75. Found: C, 42.17; H, 5.81; N, 36.9.

The treatment of X with benzaldehyde produced a 99% yield of 1-(4-benzylideneamine-5-methyl-*s*-triazol-3-yl)-3,5-dimethylpyrazole. An analytical sample was obtained by recrystallization from an ethanol–water mixture.

Anal. Calcd. for $C_{15}H_{16}N_6$: C, 64.26; H, 5.75; N, 29.98. Found: C, 64.2; H, 5.64; N, 29.7.

1-[5-Methyl-*s*-triazol-3-yl)-3,5-dimethylpyrazole (XI).—A solution of 0.78 g. of sodium nitrite in 5 ml. of water was added dropwise to a cold solution (ice–salt bath) of 2.29 g. of X in 10 ml. of water and 5 ml. of 2 *N* hydrochloric acid. The addition caused the mixture to froth vigorously and a precipitate separated. The mixture was stirred in the cold for 1 hr. and then filtered to yield 1.24 g. (70%) of a white solid melting at 150–154°. An analytical sample, m.p. 155–156°, was obtained by recrystallization from acetonitrile.

Anal. Calcd. for $C_8H_{11}N_5$: C, 54.22; H, 6.25; N, 39.53. Found: C, 54.2; H, 6.20; N, 39.6.

Acknowledgment.—The authors are indebted to Dr. L. Schieler for his helpful interest and to Dr. L. Krbechek for many helpful discussions of this work.

The Proton Magnetic Resonance Spectral Characteristics of Tricyclic Diterpenic Substances

ERNEST WENKERT, ADRIANO AFONSO, PETER BEAK,[1] RICHARD W. J. CARNEY,[2] P. W. JEFFS, AND JAMES D. MCCHESNEY[3]

Departments of Chemistry, Iowa State University, Ames, Iowa, and Indiana University, Bloomington, Indiana

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The proton magnetic resonance spectra of derivatives of dehydroabietic and podocarpic acids, of their 5-epimers, and of pimaric, sandaracopimaric, and isopimaric acids are discussed. A correlation of the chemical shifts of methyl groups and other side chains is presented. The stereochemistry of the conformationally flexible A/B *cis* compounds is analyzed.

In recent years we have become increasingly dependent on proton magnetic resonance (p.m.r.) spectra for rapid aid in the solution of structure problems in the chemistry of diterpenic substances. The spectral characteristics of the commonly encountered vinyl,[4] hydroxymethyl or acetoxymethyl,[5] and methyl[6] groups have been described and the chemical shifts and mul-

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[1] Public Health Service Predoctoral Research Fellow, 1960–1961.

[2] Public Health Service Predoctoral Research Fellow, 1961–1962.

[3] National Science Foundation Cooperative Fellow, 1962–1964.

[4] (a) E. Wenkert and P. Beak, *J. Am. Chem. Soc.*, **83**, 998 (1961). Our first-order analysis of the vinyl ABC patterns for rimuene, methyl pimarate, methyl sandaracopimarate, and methyl isopimarate has been shown by complete computational analysis [C. L. Leicht, unpublished data; R. M. Carman, *Australian J. Chem.*, **16**, 1104 (1963)] to yield incorrect coupling constants. (b) E. Wenkert, P. Beak, and P. K. Grant, *Chem. Ind.* (London), 1574 (1961). The coupling constants of the vinyl multiplets of manoyl and epimanoyl oxides, listed herein, are also suspect. The exact line positions and intensities of the reported systems are available from our laboratory on request.

[5] (a) E. Wenkert and P. Beak, *Tetrahedron Letters*, 358 (1961); (b) A. Gaudemer, J. Polonsky, and E. Wenkert, *Bull. chim. soc. France*, 407 (1964).

[6] (a) C. H. Brieskorn, A. Fuchs, J. B-s. Bredenberg, J. D. McChesney, and E. Wenkert, *J. Org. Chem.*, **29**, 2293 (1964); (b) E. Wenkert, P. W. Jeffs, and J. R. Mahajan, *J. Am. Chem. Soc.*, **86**, 2218 (1964); (c) J. C. W. Chien, *ibid.*, **82**, 4762 (1960).