[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANISIUS COLLEGE, AND THE RESEARCH LABORATORIES, INTERCHEMICAL CORPORATION]

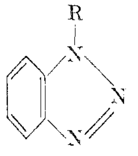
Reactions of Carbinolamines. II.[1] Acylation of 1-Hydroxymethyl-1*H*-Benzotriazole[2]

NORMAN G. GAYLORD[3] AND JAMES M. NAUGHTON

Received February 21, 1957

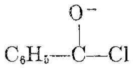
The benzoate of 1-hydroxymethyl-1*H*-benzotriazole (I) has been prepared by the reaction of I with benzoyl chloride in the presence of aqueous sodium hydroxide, with benzoic acid and *p*-toluenesulfonyl chloride in pyridine solution and with benzoic anhydride at 160°. 1-Benzoyl-1*H*-benzotriazole has been prepared from I and benzoyl chloride in the presence of pyridine or dilute hydrochloric acid. 1,1′-Methylenebisbenzotriazole was prepared by the reaction of I with benzoyl chloride at 160°. Treatment of I with acetyl chloride in the presence of pyridine yielded 1-acetyl-1*H*-benzotriazole and possibly the acetate of I.

The reaction of 1-hydroxymethyl-1*H*-benzotriazole (I) with benzoyl chloride and pyridine in dioxane solution has been shown to yield the amide 1-benzoyl-1*H*-benzotriazole (II) instead of the benzoate (III) of I.[1] The present investigation was concerned with the behavior of I under acylating conditions.



I, R = CH_2OH
II, R = COC_6H_5
III, R = CH_2OCOC_6H

The reaction of I with benzoyl chloride and pyridine in dioxane solution at 60° gave a 56% yield of the amide (II). The reaction of I with benzoyl chloride in pyridine solution at 20° gave 19% of II. No reaction was observed when I was heated in a pyridine solution at 60° for 2 hr. It has previously been postulated[1] that II may arise either by the elimination of formaldehyde to yield 1*H*-benzotriazole followed by amide formation or by the direct displacement of the methylol group by



$$C_6H_5{-}\overset{O^-}{\underset{+}{C}}{-}Cl$$

The absence of a reaction when I was heated with pyridine at 60° precludes the elimination of formaldehyde from I prior to the reaction with benzoyl chloride at either 20° or 60°. The presence of pyridine may enhance the polarization of the carbonyl group in the acyl chloride or may even participate in the ionization of the compound in the form of the acyl pyridinium chloride.

1-Benzoyloxymethyl-1*H*-benzotriazole (III) was prepared by a Schotten-Baumann reaction of I with benzoyl chloride in the presence of a 10% sodium hydroxide solution, in 40% yield at 20° and in 26.5% yield at 45–65°. III was identified by elemental analysis, an infrared absorption band at 5.75 μ, characteristic of an ester group, and its behavior on reduction with lithium aluminum hydride and sodium borohydride.[4] Whereas I and II yield the picrate of benzotriazole,[1] attempts to prepare a picrate from III were unsuccessful.

The Schotten-Baumann reaction with I at 60° gave a 52% yield of benzotriazole without the formation of III. Treatment of I with a dilute sodium hydroxide solution gave 8% of benzotriazole at 20° and 91% at 60°, with the residual recovered material being unreacted I.

The loss of formaldehyde from I at 60° in the presence of base is responsible for the failure to obtain III in the Schotten-Baumann reaction. The isolation of benzotriazole instead of II under these conditions is probably due to the hydrolysis of the acyl chloride. At 20° I is not as readily decomposed by the base, so that esterification occurs in the presence of benzoyl chloride. At 45° the yield of III is reduced as a result of the considerably greater decomposition of I and/or benzoyl chloride.

The reaction of I with benzoyl chloride in the presence of dilute hydrochloric acid in dioxane at 20° gave 39% of II. At 60° the only product isolated besides I was benzoic acid. Dilute hydrochloric acid with I in dioxane at 60° gave no reaction. Apparently I is not attacked by dilute acid at 60° although the elimination of formaldehyde occurs in the presence of base. However, at 60° the acid hydrolyzes the benzoyl chloride so that reaction with I does not occur. At 20° neither hydrolysis of the acid chloride nor attack on I occurs to an extent to interfere with the formation of II by a reaction which may be analogous to that which occurs in the presence of pyridine.

Treatment of I with benzoyl chloride for 1 hr. at 160° gave a 36% yield of a condensation product, 1,1′-methylenebisbenzotriazole (IV), previously prepared from benzotriazole and 1-chloromethyl-

---

(1) Part I: N. G. Gaylord, *J. Am. Chem. Soc.*, **76**, 285 (1954).

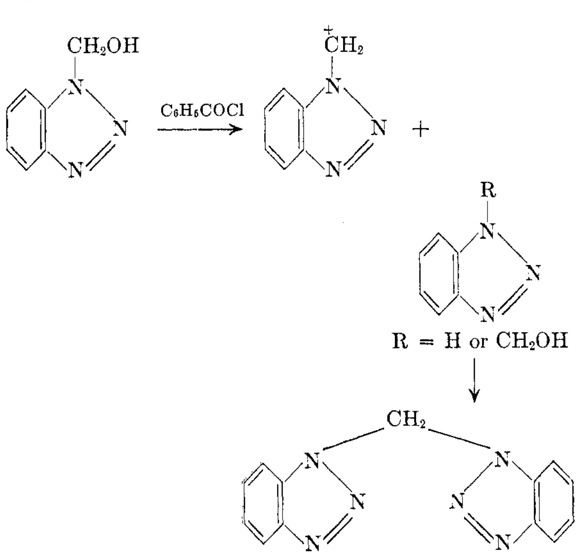
(2) Abstracted in part from the M.S. thesis of J. M. Naughton, Canisius College, June 1955.

(3) To whom inquiries should be sent. Present address: Interchemical Corporation, The Research Laboratories, 432 W. 45th St., New York 36, N. Y.

(4) N. G. Gaylord and D. J. Kay, unpublished work.

1*H*-benzotriazole with sodamide in toluene.[5] No isomeric 1,2-methylenebisbenzotriazole, obtained in 4% yield in the latter reaction, was identified in the present case. No picrate could be obtained from IV.

The formation of the condensation product (IV) may be analogous to the curing mechanism of urea-formaldehyde and melamine-formaldehyde resins. Thus, the elimination of formaldehyde and water between two molecules of the *N*-methylol compound would yield the methylene derivative. Alternatively, the elimination of water between molecules of I and benzotriazole would yield IV. The benzotriazole may arise through the thermal decomposition of I. A carbonium ion, arising by the action of benzoyl chloride on I, may be an intermediate in the reaction as shown.



IV

The reaction of I with benzoic anhydride at 160° gave III in 24% yield. Treatment of I with benzoic acid and *p*-toluenesulfonyl chloride in pyridine solution[6] gave a 27% yield of III.

An alcoholysis reaction between I and ethyl benzoate with acid catalysis in dioxane solution was unsuccessful.

Treatment of I with acetyl chloride and pyridine in dioxane solution at 60° yielded 30% of the amide, 1-acetyl-1*H*-benzotriazole. An impure liquid fraction, isolated in 8% yield, had an elemental analysis which indicated the probable presence of the ester. The amide gave the picrate of benzotriazole.

EXPERIMENTAL

1-Hydroxymethyl-1H-benzotriazole (I), m.p. 148–149°, was prepared in 84% yield from benzotriazole, formalin, and acetic acid, according to the procedure of Burckhalter, Stephens, and Hall.[5]

Reaction of I with benzoyl chloride in pyridine at 60°, according to the procedure of Gaylord,[1] gave 1-benzoyl-1*H*-benzotriazole (II), m.p. 110–112°, in 56% yield.

Reaction of I with benzoyl chloride in pyridine at 20°. I (14.6 g., 0.098 mole) was dissolved in 75 ml. of pyridine and the solution was cooled to 12°. Benzoyl chloride (21.1 g., 0.15 mole) was added dropwise over a period of 1 hr. and the temperature was raised to 20°. A white precipitate formed during the addition. The reaction mixture was diluted with 350 ml. of ether and stirred for 30 min. while the flask was immersed in an ice bath. The ethereal solution was decanted from the precipitate and washed successively with aqueous solutions of sodium carbonate, hydrochloric acid, sodium bicarbonate, and water. The volatile solvents were removed under vacuum and the residual solid, 14.6 g., was recrystallized from ethyl acetate to yield 4.0 g. (18.5% yield) of II, m.p. 110–112° (reported[1] m.p. 110–113°). A mixed melting point with authentic material showed no depression while a mixed melting point with benzotriazole, m.p. 98°, was m.p. 70–85°.

The attempted *reaction of I with pyridine at 60°* for 2 hr. resulted in the quantitative recovery of I.

Reaction of I with benzoyl chloride in sodium hydroxide solution. A. At 60°. A slurry of 29.1 g. (0.19 mole) of I in 50 ml. of water was heated with stirring to 60°. While the temperature was held at 60°, 200 g. of a 10% sodium hydroxide solution and 42.2 g. of benzoyl chloride were simultaneously added over 1 hr. at such a rate that three drops of the basic solution were added for each drop of acyl chloride. A white precipitate formed during the addition. The mixture was stirred for an additional 20 min. until the temperature dropped to 40°. After standing overnight the mixture was filtered to yield 40 g. of crude, air-dried product. The crude material was recrystallized once from ethyl acetate and twice from a benzene-hexane mixture to yield 12 g. (52%) of benzotriazole, m.p. 95°, no depression on admixture with authentic material.

B. At 20°. The slurry of I in water was cooled to 5°. During the first 0.5 hr. of the addition of sodium hydroxide and benzoyl chloride the temperature rose to 20° and was held at 20° for the remaining 0.5 hr. The crude, air-dried product, 40 g., was recrystallized from 75 g. of ethyl acetate to yield 19.5 g. (39.5%) of III, m.p. 93–94°, unchanged after recrystallization from hexane. Admixture with benzotriazole gave m.p. 70–84° and admixture with II gave m.p. 78–100°.

Anal. Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.35; N, 16.61. Found: C, 66.19; H, 4.20; N, 16.69.

The infrared absorption spectrum of III showed a strong band at 5.75 μ, characteristic of an ester grouping.

C. At 45–65°. I (29.1 g., 0.19 mole) was dissolved in 200 g. of 10% sodium hydroxide (0.5 mole) solution at 25° and cooled at 20°. Benzoyl chloride (42.2 g., 0.3 mole) was added dropwise over 45 min. during which time the temperature rose to 45°. The reaction mixture was maintained at 45° for an additional 45 min. after the addition was complete, and then the temperature was raised to 65° over a 15 min. period. The mixture was cooled to 25°, filtered, and the precipitate was washed with ice cold water and air dried to yield 35 g. of crude product. Recrystallization from 125 ml. of ethanol gave 22.0 g. of material which was dissolved in 70 g. of ethyl acetate and precipitated with 65 g. hexane, cooled to 10° and filtered to yield 13.0 g. (26.4%) of white needles, m.p. 93–94°, no depression on admixture with III obtained in 20° reaction.

Reaction of I with sodium hydroxide. A. At 60°. I (14.6 g.) was dissolved in 100 g. of 10% sodium hydroxide solution and heated in a water bath at 60° for 2 hr. The solution was cooled to 25° and treated with 75 ml. of 10% hydrochloric acid to adjust the *p*H to 6.0. The mixture was cooled to 5° and filtered to yield 11.0 g. (91%) of benzotriazole, m.p. 98°.

B. At 20°. The solution obtained after holding I in aqueous sodium hydroxide for 2 hr. at 20° was treated with 85 ml.

---

[5] J. H. Burckhalter, V. C. Stephens, and L. A. R. Hall, *J. Am. Chem. Soc.*, **74**, 3868 (1952).

[6] J. H. Brewster and C. J. Ciotti, Jr., *J. Am. Chem. Soc.*, **77**, 6214 (1955).

of 10% hydrochloric acid to adjust the pH to 3.0. The mixture was cooled to 10° and filtered to yield 11.5 g., m.p. 142–145°. Recrystallization from water gave a 62% recovery of I. The filtrate from the recrystallization yielded 2.0 g. (8%) of benzotriazole.

Reaction of I with benzoyl chloride in hydrochloric acid. A. At 20°. I (29.1 g., 0.19 mole) was mixed with 100 ml. of dioxane and the slurry was cooled to 12°. A 10% hydrochloric acid solution, 200 ml., and 42.2 g. of benzoyl chloride were added dropwise over a period of 45 min. at a 3:1 drop ratio, respectively, while the temperature was maintained at 20°. The mixture was stirred for an additional 15 min., filtered, and air dried to yield 34 g. of crude product. Recrystallization from ethyl acetate gave 17 g. (39%) of II, m.p. 112–113°, no depression on admixture with authentic material.

B. At 60°. I (14.6 g.) was dissolved in 150 ml. of dioxane by heating at 53°. The temperature was raised to 60° and 100 ml. of a 10% hydrochloric acid solution and 21.1 g. of benzoyl chloride were added over 1 hr. while maintaining this temperature. The solution was cooled to 30° while stirring for 1 hr. and partially concentrated by blowing air over the solution at 25°. The mixture was cooled to 5°, filtered, and the precipitate was air dried to yield 12 g. of crude material. Recrystallization from benzene gave 3.5 g. (19%) of benzoic acid, m.p. 121–123°. The filtrate from the reaction mixture was evaporated with air to yield crude I which was recrystallized from ethyl acetate.

Reaction of I with hydrochloric acid at 60°. A solution of 14.6 g. of I in 100 ml. of dioxane and 25 ml. of a 10% hydrochloric acid solution was heated for 2 hr. at 60°. The solution was cooled to 25° and air evaporated to yield 15 g. of crude I, recrystallized from ethyl acetate to yield 12 g. (82%) of I, m.p. 146–147°.

Reaction of I with benzoyl chloride. A mixture of 24.8 g. (0.17 mole) of I and 25.0 g. (0.17 mole) of benzoyl chloride was heated in an oil bath at 160° for 1 hr. The clear melt partially crystallized on cooling to room temperature. After the addition of 750 ml. of ether the mixture was stirred for 1 hr. in an ice bath. The ethereal solution was decanted and washed successively with aqueous solutions of sodium carbonate, hydrochloric acid, sodium bicarbonate, and water. After removal of the ether under vacuum the residue was recrystallized several times from an aqueous ethanol solution to yield 2.0 g. of IV, m.p. 191–192°. The residue, 15.0 g., from the original reaction mixture was washed as above to yield 10 g. of crude material which was recrystallized from ethyl acetate. A total of 5.5 g. (36% yield) of IV was obtained. On recrystallization from dilute ethanol the product had m.p. 191–193° (reported[5] m.p. 192–193°).

Anal. Calcd. for $C_{13}H_{10}N_6$: C, 62.39; H, 4.03; N, 33.48. Found: C. 62.45; H, 3.91; N, 33.43.

Reaction of I with benzoic anhydride. A mixture of 24.8 g. (0.17 mole) of I and 38 g. (0.17 mole) of purified benzoic anhydride was heated in an oil bath at 160° for 1 hr. The crude product was crystallized from dilute ethanol to yield 5.5 g. of product, m.p. 88–92°. Recrystallization from dilute ethanol gave 5.0 g. (24%) of III, m.p. 92–94°, no depression on admixture with the product from the Schotten-Baumann reaction at 20°, and benzoic acid.

Reaction of I with benzoic acid and p-toluenesulfonyl chloride. A solution of 10 g. (0.067 mole) of I in 50 ml. of pyridine was added slowly with stirring to a mixture of 23.6 g. (0.124 mole) of *p*-toluenesulfonyl chloride and 7.6 g. (0.062 mole) of benzoic acid in 100 ml. of pyridine. The temperature was maintained at 5–10° during the addition and for an additional 1.5 hr. The reaction mixture was poured into 3 volumes of ice water and the precipitated solid was filtered and air dried to yield 2.6 g. of III. The filtrate was concentrated by blowing air over the surface of the solution to yield an additional 1.0 g. of III, total 3.6 g. (21.4% yield). Acidification of the filtrate to pH 2 resulted in the precipitation of 3.15 g. (31.5%) of I.

When the reaction was carried out with 25.4 g. (0.134 mole) of *p*-toluenesulfonyl chloride and 8.1 g. (0.067 mole) of benzoic acid in 50 ml. of pyridine, a total of 4.7 g. (27.4% yield) of III was obtained.

Reaction of I with acetyl chloride in pyridine. A solution of 23.5 g. (0.3 mole) of acetyl chloride in 25 ml. of dioxane was added dropwise over 0.5 hr. to a solution of 29.1 g. of I in 100 ml. of dioxane and 31.6 g. (0.4 mole) of pyridine. The temperature was maintained at 20° during the addition and then the mixture was heated at 55° for 1 hr. The mixture was diluted with 750 ml. of ether and stirred for 0.5 hr. at 5° in an ice bath. The ethereal solution was decanted and washed successively with aqueous solutions of sodium carbonate, hydrochloric acid, sodium bicarbonate, and water. After drying over calcium chloride the ether was evaporated to yield 16.4 g. of crude product which was distilled and collected at 95–115° (0.5 mm.). A white solid (7.5 g., 24%) distilled first, followed by 6.5 g. of a clear liquid. The solid had m.p. 49–51° and on recrystallization had m.p. 50–51°.

Anal. Calcd. for $C_8H_7N_3O$: C, 59.63; H, 4.35; N, 26.09. Found: C, 59.42; H, 4.41; N, 25.87.

Redistillation of the liquid gave an additional 2.0 g. (total yield 30%) of *1-acetyl-1H-benzotriazole* and 3.0 g. (8%) of liquid, b.p. 112–120° (0.3 mm.). Analysis of the liquid fraction indicated the probable presence of the ester *1-acetoxymethyl-1H-benzotriazole.*

Anal. Calcd. for $C_9H_9N_3O_2$: C, 56.54; H, 4.71; N, 21.99. Found: C, 57.60; H, 4.50; N, 23.10.

Acknowledgment. The assistance of Daniel J. Kay and Karl Schmidt in portions of the experimental work is gratefully acknowledged.

NEW YORK, N. Y.

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO., INC., EASTERN LABORATORY]

Reduction of Nitroparaffins by Alkylation. I. Aklylation with Trialkyl Oxonium Salts[1]

L. GUY DONARUMA[2]

Received February 22, 1957

The reduction of the sodium *aci* salts of nitrocyclohexane, nitrocyclopentane, and 2-nitropropane by alkylation is described. The preparation of trialkyl oxonium salts is discussed. The preparation and certain reactions of some cyclohexanone oxime-*O*-alkyl ethers is described.

The oxygen alkylation of nitroparaffin *aci* salts (I) has been studied by various investigators.[3–6] The usual products of the reaction are an oxime (IV) and a carbonyl compound (V). The nature of the