from methanol to give 3.5 g. (91%) of crystals, m.p. 119–120°.

Anal. Calcd. for $C_{20}H_{22}O_9$: C, 59.10; H, 5.46. Found: C, 59.19; H, 5.51.

Triethylene Glycol Diisodehydroacetate.—A mixture of 4 g. (0.0215 mole) of isodehydroacetyl chloride and 1.5 g. (0.010 mole) of triethylene glycol was heated in an oil-bath at 120–135° for six hours. The residue, recrystallized from methanol, gave 4.0 g. (89%) of crystals, m.p. 108°.

Anal. Calcd. for $C_{22}H_{26}O_{10}$: C, 58.66; H, 5.82. Found: C, 59.10; H, 6.02.

Thiodiethylene Glycol Diisodehydroacetate.—A mixture of 1.3 g. (0.011 mole) of thiodiethylene glycol and 4.1 g. (0.022 mole) of isodehydroacetyl chloride was heated for six hours in an oil-bath. The reaction product was recrystallized from benzene–ligroin to give 2.7 g. (60%) of crystals, m.p. 80–81° (from toluene).

Anal. Calcd. for $C_{20}H_{22}O_8S$: C, 56.88; H, 5.25. Found: C, 56.69; H, 5.26.

Pentaerythritol Tetraisodehydroacetate.—A mixture of 0.54 g. (0.0040 mole) of pentaerythritol and 3.0 g. (0.0166 mole) of isodehydroacetyl chloride was heated to 150° and cooled to deposit a solid residue which was recrystallized from acetic acid to give 2.3 g. (77%) of crystals, m.p. 225–227°.

Anal. Calcd. for $C_{37}H_{36}O_{16}$: C, 60.32; H, 4.93. Found: C, 60.32; H, 5.03.

Reaction of Hydrazine Hydrate with Ethyl Isodehydroacetate.—To 15.0 g. (0.0765 mole) of ethyl isodehydroacetate cooled in an ice-bath was slowly added 7.5 g. (0.15 mole) of hydrazine hydrate. After one hour, 25 ml. of water was added to precipitate a white solid which was collected, dried, and recrystallized from ethanol to give 2.8 g. (18%) of 3-methyl-5-pyrazolone, m.p. 216–218° (cor.); reported m.p. 219°.[9]

Anal. Calcd. for $C_4H_6ON_2$: C, 48.98; H, 6.17; N, 28.56. Found: C, 49.22; H, 6.11; N, 28.62.

The compound gives a positive ferric chloride enol test and no depression of m.p. on admixture with a sample of 3-methyl-5-pyrazolone, m.p. 216–218°, prepared from ethyl acetoacetate and dihydrazine sulfate.[10] The monoacetyl derivative was prepared from each sample,[11] m.p.'s and mixed m.p.'s 153–154° (cor.); reported[10] m.p. 140°.

Anal. Calcd. for $C_6H_8O_2N_2$: N, 19.98. Found: N, 19.92.

---

(9) F. K. Beilstein, "Handbuch der organischen Chemie," J. Springer, Berlin, 1936, Vol. XXIV, p. 19.

(10) L. Knorr, *Ber.*, **29**, 253 (1896).

(11) T. Curtius, *J. prakt. Chem.*, **50**, 511 (1894).

LOUISVILLE, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Conjugate Addition Reactions of Azoles: 1,2,3-Triazole and Benzotriazole

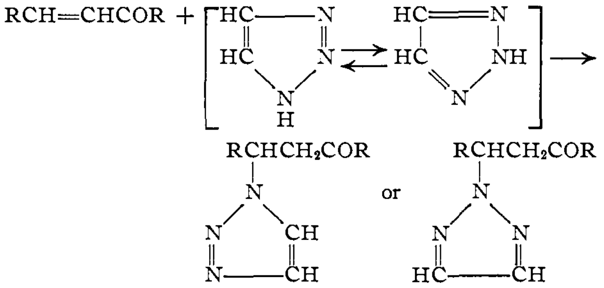
BY RICHARD H. WILEY, N. R. SMITH, DAVID M. JOHNSON[1] AND JAMES MOFFAT

RECEIVED JANUARY 27, 1954

The addition of azoles having an unsubstituted, exocyclic imino group to conjugated, unsaturated systems is presented for additions of 1,2,3-triazole and benzotriazole to acrylic acid, acrylamide, acrylonitrile, crotonic acid, benzalacetophenone, *p*-methoxybenzalacetone, benzalacetone, dibenzalacetone and cinnamaldehyde. Ultraviolet absorption data for the five benzotriazole adducts show clearly the double maxima at 255 mμ and 283 mμ characteristic of 1-substituted benzotriazoles and the data for the benzalacetophenone adducts from both benzotriazole and triazole show the absorption maximum at 245 mμ characteristic of the carbonyl group conjugated with the benzene ring. On this basis, the products are assigned β-(1-benzotriazolyl or 1-triazolyl) carbonyl (or related) structures.

The experimental data presented in this paper establish the 1,4-addition of 1,2,3-triazole to acrylic acid, benzalacetophenone (chalcone), benzalacetone and dibenzalacetone (1,5-diphenylpentadieneone-3); the 1,4-addition of benzotriazole to acrylic acid, crotonic acid, benzalacetophenone (chalcone), *p*-methoxybenzalacetone and acrylonitrile; and the simultaneous 1,4- and 1,2-addition of benzotriazole to cinnamaldehyde. The addition reaction is carried out by warming the reactants together in the presence of pyridine or Triton B (trimethylbenzylammonium hydroxide) as the basic catalyst.

The structure of the addition product formed on addition of an iminoazole such as 1,2,3-triazole or benzotriazole to an unsaturated system is complicated by the possibility for linkage at either of two different nitrogen atoms. Thus, with 1,2,3-triazole addition can occur to give either a 1- or a 2-substituted triazole.



A B

Of various methods available for establishing the structure of a product obtained when such isomerism is possible, an analysis of ultraviolet absorption spectra is most direct. The ultraviolet absorption data summarized in Table I establish the 1-benzotriazole structure and the presence of the carbonyl group in products obtained in this study. The ultraviolet absorption spectra of 1- and 2-alkyl benzotriazoles have been shown previously[2,3] to differ. The 1-substituted types show double maxima at 255 mμ (log ε 3.81) and 283 mμ (log ε 3.68) and the 2-substituted types show a single maximum at 275 mμ (log ε 3.90). Our data show that the benzotriazole adducts with acrylic acid, acrylonitrile, acrylamide, crotonic acid and cinnamaldehyde, are unmistakably of the 1-substituted type. All have two characteristic maxima with similar extinction coefficients. Perhaps because of a slightly greater resolution than was obtained previously we observed a double maxima at each of the principal maxima for each of these compounds. The benzotriazole and 1,2,3-triazole adducts from benzalacetophenone

---

(1) Office of Ordnance Research graduate research assistant.

(2) F. Krollpfeiffer, H. Pötz and A. Rosenberg, *Ber.*, **71B**, 596 (1938).

(3) H. Specker and H. Gawrosch, *ibid.*, **75B**, 1338 (1942).

show absorption maxima at 245 mμ and 280 mμ at the same wave lengths as does benzylacetophenone, 238 mμ (log ε 4.09) and 280 mμ (log ε 3.18).[4] The absorption at 245 is assigned to the common feature of these compounds known to absorb in this region—the carbonyl group conjugated with the benzene ring. The 1,2,3-triazole adducts with benzalacetone and dibenzalacetone show only the characteristic triple maxima of the isolated benzene ring in the 250–270 mμ range. There is no known method for distinguishing 1- from 2-alkyl-1,2,3-triazoles. The products reported herein are tentatively assigned the 1-alkyl structure by analogy with the benzotriazoles.

TABLE I

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF BENZOTRIAZOLE AND TRIAZOLE ADDUCTS IN METHANOL

Compound, benzotriazole adducts from	Wave length, mμ	Extinction coefficient (log ε)
Acrylic acid	257	3.86
	280	3.70
Acrylonitrile	256	3.84
	281	3.66
Acrylamide	259	3.81
	279	3.66
Crotonic acid	255	3.84
	278	3.64
Cinnamaldehyde	258	4.10
	276	3.95
Benzalacetophenone	244	4.31
	280 (shoulder)	3.75
1,2,3-Triazole adducts from		
Benzalacetophenone	245	4.13
	282	3.15
Benzalacetone	254	2.98
	258	2.20
	264	2.13
Dibenzalacetone	252	2.39
	258	2.53
	264	2.43

Acknowledgment.—This research was completed under Contract DA-33-008 ord-734 between the Office of Ordnance Research and the University of Louisville. The authors gratefully acknowledge this support.

Experimental[5]

The 1,2,3-triazole used in these studies was prepared by decarboxylation of 1,2,3-triazole-4-carboxylic acid.[6] This acid was obtained by oxidation of the corresponding aldehyde.[7] Since this oxidation reaction has not been described before details are given. The acrylic acid,[8] crotonic acid[8] and Triton B[8] (40% aqueous) were used as supplied. Benzotriazole and the unsaturated aldehydes and ketones were obtained from commercial sources.

β-[1'-(1,2,3-Triazolyl)]-propionic Acid.—A mixture of 0.5 g. (0.007 mole) of 1,2,3-triazole, 0.5 g. (0.007 mole) of acrylic acid and five drops of pyridine was heated in a boiling water-bath for six hours. The solution was dissolved in 25 ml. of water containing 10 drops of concd. hydrochloric acid, decolorized and filtered. The filtrate was evaporated to dryness and the residue extracted with methyl ethyl ketone. Evaporation of the methyl ethyl ketone left 0.6 g. of product which was recrystallized from ethyl acetate to give 0.25 g. (25% of the theoretical amount) of β-[1'-(1,2,3-triazolyl)]-propionic acid, m.p. 126–131°.

Anal. Calcd. for $C_5H_7O_2N_3$: C, 42.55; H, 5.00; neut. equiv., 141.13. Found: C, 42.70; H, 4.90; neut. equiv., 142.3.

β-Phenyl-β-[1'-(1,2,3-triazolyl)]-propiophenone.—A mixture of 2.0 g. (0.01 mole) of benzalacetophenone, 0.7 g. (0.01 mole) of 1,2,3-triazole and one drop of Triton B was warmed gently over an open flame for ten minutes and diluted with ether to precipitate 1.5 g. (56% of the theoretical amount) of β-phenyl-β-[1'-(1,2,3-triazolyl)]-propiophenone, m.p. 146–146.5° after recrystallization from methanol and then from ethanol. The compound is soluble in benzene, carbon tetrachloride, methanol and ethanol; insoluble in ether and petroleum ether.

Anal. Calcd. for $C_{17}H_{15}ON_3$: C, 73.62; H, 5.45; N, 15.15. Found: C, 73.61; H, 5.48; N, 15.00.

1-Phenyl-1-[1'-(1,2,3-triazolyl)]-butanone-3.—A mixture of 0.84 g. (0.012 mole) of 1,2,3-triazole, 1.78 g. (0.012 mole) of benzalacetone and one drop of Triton B was heated three hours in a boiling water-bath, allowed to stand ten hours, and diluted with 50 ml. of ether to precipitate 0.50 g. (19% of the theoretical amount) of 1-phenyl-1-[1'-(1,2,3-triazolyl)]-butanone-3, m.p. 106–107° after recrystallization from carbon tetrachloride.

Anal. Calcd. for $C_{12}H_{13}ON_3$: C, 66.95; H, 6.09; N, 19.52. Found: C, 67.21; H, 6.11; N, 19.52.

1,5-Diphenyl-1,5-di-[1'-(1,2,3-triazolyl)]-pentanone-3.—A mixture of 1.38 g. (0.02 mole) of 1,2,3-triazole and 2.34 g. (0.01 mole) of 1,5-diphenylpentadienone-3 was heated in a boiling water-bath to solution. Three drops of Triton B were added and the heating continued for six hours. During this time the mixture solidified. The solid was washed with ether to remove starting materials and recrystallized from ethanol to give 0.50 g. (13.5%) of 1,5-diphenyl-1,5-di-[1'-(1,2,3-triazolyl)]-pentanone-3, m.p. 160–165°.

Anal. Calcd. for $C_{21}H_{20}ON_6$: C, 67.72; H, 5.41; N, 22.57. Found: C, 67.83; H, 5.63; N, 22.72.

β-(1'-Benzotriazolyl)-propionic Acid.—A mixture of 12 g. (0.1 mole) of benzotriazole and 7.2 g. (0.1 mole) of acrylic acid was heated to solution. Fifty drops of pyridine were added and the resulting solution heated five hours in a boiling water-bath. The resulting mixture was poured onto 200 ml. of water, heated to solution, acidified with 5 ml. of dilute hydrochloric acid, treated with Norite, filtered and cooled to precipitate the product. Recrystallization from water gave 9.5 g. (49% of the theoretical amount) of β-(1'-benzotriazolyl)-propionic acid, m.p. 120–121°.

Anal. Calcd. for $C_9H_9O_2N_3$: C, 56.54; H, 4.75; N, 21.98; neut. equiv., 191.2. Found: C, 56.54; H, 4.99; N, 22.22; neut. equiv., 191.9.

β-[1'-Benzotriazolyl]-propionamide.—A mixture of 1.19 g. (0.01 mole) of benzotriazole, 0.71 g. (0.01 mole) of acrylamide and five drops of Triton B was heated for five hours in a boiling water-bath. Diethyl ether was used to extract the cooled reaction mixture leaving a solid which was soluble in ethanol and water and insoluble in carbon tetrachloride. Recrystallization from dioxane gave 0.70 g. (36% of the theoretical amount) of β-[1'-benzotriazolyl]-propionamide, m.p. 140–142°.

Anal. Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30. Found: C, 56.88; H, 5.04.

The same product was obtained by converting β-[1'-benzotriazolyl]-propionic acid to the amide *via* the acid chloride[9] as judged by lack of depression in melting points of mixtures of the two.

β-(1'-Benzotriazolyl)-butyric Acid.—A mixture of 6.0 g. (0.05 mole) of benzotriazole and 4.3 g. (0.05 mole) of cro-

---

[4] N. H. Cromwell and H. Hoeksema, THIS JOURNAL, **71**, 708 (1949).

[5] Analyses by Micro Tech Laboratories. All melting points are corrected.

[6] O. Dimroth, *Ber.*, **35**, 1045 (1902).

[7] R. Hüttel, *ibid.*, **74**, 1680 (1941). The authors are indebted to General Aniline and Film Corporation for generously supplying samples of propargyl alcohol.

[8] The authors are indebted to the B. F. Goodrich Company for generously supplying samples of acrylic acid; the Tennessee Eastman Company for generously supplying samples of crotonic acid; and the Rohm and Haas Company for generously supplying samples of Triton B.

[9] The authors are indebted to Mr. Karl Hussung for carrying out this reaction.

tonic acid was heated to solution in a boiling water-bath. After adding 25 drops of pyridine the heating was continued for eleven hours. The resulting solution was poured onto water, heated to solution, acidified with 5 ml. of dil. hydrochloric acid, treated with Norite, filtered, and cooled to precipitate the product. Recrystallization from water gave 4.2 g. (40.7% of the theoretical amount) of β-(1′-benzotriazolyl)-butyric acid, m.p. 150–152°.

Anal. Calcd. for $C_{10}H_{11}O_2N_3$: C, 58.53; H, 5.40; N, 20.48; neut. equiv., 205.2. Found: C, 58.20; H, 5.48; N, 20.58; neut. equiv., 205.4.

β-Phenyl-β-(1′-benzotriazolyl)-propiophenone.—A mixture of 1.19 g. (0.01 mole) of benzotriazole, 2.08 g. (0.01 mole) of benzalacetophenone and one drop of Triton B was melted together, heated 1.5 hours on a boiling water-bath, let stand 12 hours, and diluted with ether. Addition of petroleum ether precipitated 1.99 g. (61% of the theoretical amount) of β-phenyl-β-(1′-benzotriazolyl)-propiophenone, m.p. 106–107° after recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{17}ON_3$: C, 77.04; H, 5.23; N, 12.84. Found: C, 76.96, H, 5.41; N, 12.88.

1-(*p*-Methoxyphenyl)-1-(1′-benzotriazolyl)-butanone-3.—A mixture of 1.19 g. (0.01 mole) of benzotriazole, 1.76 g. (0.01 mole) of *p*-methoxybenzalacetone and one drop of Triton B was melted over a free flame and heated six hours on a boiling water-bath. The mixture was cooled, taken up in ether, and diluted with petroleum ether to precipitate 1.13 g. (38% of the theoretical amount) of 1-(*p*-methoxyphenyl)-1-(1′-benzotriazolyl)-butanone-3, m.p. 93–94° after recrystallization from ethanol.

Anal. Calcd. for $C_{17}H_{17}O_2N_3$: C, 69.13; H, 5.80; N, 14.23. Found: C, 69.13; H, 6.02; N, 14.32.

3-Phenyl-1,3-di-(1′-benzotriazolyl)-propanol-1.—A mixture of 1.19 g. (0.01 mole) of benzotriazole, 1.32 g. (0.01 mole) of cinnamaldehyde and one drop of Triton B was melted over a free flame and heated six hours in a boiling water-bath. Addition of 40 ml. of ether to the cooled reaction mixture precipitated 0.85 g. (46% of the theoretical amount) of 3-phenyl-1,3-di-(1′-benzotriazolyl)-propanol-1, m.p. 127° after recrystallization from benzene–carbon tetrachloride. The product is soluble in benzene and ethanol, and is insoluble in carbon tetrachloride and ether.

Anal. Calcd. for $C_{21}H_{18}ON_6$: C, 68.09; H, 4.90; N, 22.69. Found: C, 67.83; H, 5.13; N, 22.84.

β-(1′-Benzotriazolyl)-propionitrile.—A mixture of 1.19 g. (0.01 mole) of benzotriazole and 0.53 g. (0.01 mole) of acrylonitrile was heated to solution. Five drops of Triton B were added and the mixture heated on a water-bath for five hours. The oily reaction mixture was poured into 30 ml. of ether to precipitate the product as a white solid, soluble in acetone, hot water, ethanol, benzene, carbon tetrachloride and dioxane; insoluble in ether and petroleum ether. After three recrystallizations from carbon tetrachloride, there was obtained 0.40 g. (23–25% of the theoretical amount) of β-benzotriazolylpropionitrile, m.p. 79–80°.

Anal. Calcd. for $C_9H_8N_4$: C, 62.77; H, 4.68; N, 32.54. Found: C, 63.21; H, 4.55; N, 32.55.

1,2,3-Triazole-4-carboxylic Acid.—To a solution of 9.30 g. (0.097 mole) of 1,2,3-triazole-4-carboxyaldehyde in 150 ml. of hot water was added with stirring a solution of 10.70 g. (0.0677 mole) of potassium permanganate in 125 ml. of water. The resulting solution was heated to boiling and filtered hot. The precipitate was washed with water. The filtrate was then made basic with solid potassium hydroxide and concentrated to a volume of 75 ml., acidified with excess hydrochloric acid and cooled to precipitate the product. After recrystallization from water there was obtained 6.30 g. (83.2% of the theoretical amount) of 1,2,3-triazole-4-carboxylic acid, m.p. 218–219°, neut. equiv., 111.3; reported[7] m.p. 219°.

Ultraviolet Absorption Data.—Ultraviolet absorption measurements were made with a Beckman DU photoelectric spectrophotometer using 1.00-cm. silica cells and hydrogen and tungsten discharge lamps as light sources. The measurements were made with methanol solutions.

LOUISVILLE, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Condensations by Sodium. XXXVII. The Dimetalation of Benzene, Thiophene, *p-t*-Butylphenol, Isopropylbenzene and *sec*-Butylbenzene and the Effect of Alkoxides on the *meta:para* Ratio for Benzene[1,2]

BY AVERY A. MORTON AND CHESTER E. CLAFF, JR.

RECEIVED MARCH 8, 1954

Amylsodium dimetalates benzene chiefly in the *meta* position but the ratio of *meta* to *para* can be altered by the alkoxide which is associated with the reagent. Thiophene is easily dimetalated in the 2,5-positions. *t*-Butylphenoxide is attacked in the 2,6-position. Isopropylbenzene and *sec*-butylbenzene are dimetalated in the 3,5-positions.

Introduction

Previous work[3] has shown that alkoxides affect greatly the degree and kind of metalation of *t*-butylbenzene. The present paper describes the variations achieved in yield and in the excess of *meta* over *para* dimetalation of benzene and gives a simple explanation for these effects. In addition, it reports that thiophene is dimetalated in the 2,5-positions, *t*-butylphenol in the 2,6-positions and isopropylbenzene and *sec*-butylbenzene in the 3,5-positions. These metalations and the previous work[4] show that amylsodium is an excellent agent for the dimetalation of hydrocarbons and other compounds.

The general method was to prepare amylsodium from amyl chloride and sodium metal, then convert some of this sodium reagent to alkoxide by addition of an alcohol or add a lithium or potassium alkoxide prepared separately if the cation influence was under study. Finally the compound to be dimetalated was added. Usually the reaction was at 60°. After the product was carbonated the dicarboxylic acid was precipitated by addition of mineral acid to the aqueous solution of the salts. The ratio of *meta* to *para* phenylenedisodium was determined by the convenient method of Bryce-Smith and Turner[5] which consists of esterifying with methanol–sulfuric acid and crystallizing the pure *para* and *meta* compounds from methanol. With the sodium reagent, part of the more soluble

---

[1] This work was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] A portion of this work was presented at the Boston Meeting of the American Chemical Society, 1951.

[3] A. A. Morton, C. E. Claff, Jr., and F. W. Collins, unpublished.

[4] A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., THIS JOURNAL, **65**, 1339 (1943).

[5] D. Bryce-Smith and E. E. Turner, *J. Chem. Soc.*, 861 (1953)