800 cm.$^{-1}$ of which the higher frequency component is invariably the more intense. The absorptions at or near 1622 and 1571 cm.$^{-1}$ in purine accord-to this interpretation are characteristic of the pyrimidine-like ring common to purine, pyrimidine, and quinazoline. In pyrimidine itself,[2] strong or very strong peaks are found at 1610 and 1569 cm.$^{-1}$; in quinazoline,[4] strong absorptions, reasonably stable against substitutions, are found at 1622 and 1566 cm.$^{-1}$. Bellamy[8] has criticized the assignment of the higher of these two frequencies as a characteristic C=C and/or C=N ring vibration on the substantial grounds that such a frequency was observed previously in pyrimidines which in many cases involved amino-substitution, an objection which does not apply here. We are, however, at a loss to explain the disappearance of this band in the work of Short and Thompson.[3]

Experimental

Preparation of Purines.—The mono- and disubstituted purines were prepared previously in this Laboratory.[9] The salts were converted to free bases for the purpose of this study. Purine was prepared by the procedure of Albert and Brown.[10] All samples were tested for homogeneity by paper chromatography according to the procedure of Vischer and Chargaff.[11]

Preparation of Samples.—The free bases of all compounds were examined as solids sublimed on rock salt crystals at 10^{-5} mm. pressure in a manner similar to that of Blout and Fields.[6] Sublimation data are included in Table I.

Instrumentation and Measurement.—The instrument used was a Perkin–Elmer model 12C spectrophotometer modified as described by Culbertson, *et al.*[5] The spectra were obtained by single beam operation of a NaCl or LiF prism followed by a point by point comparison of the spectrum of the sample with that of a blank. The single beam method was preferable to the double beam because of the higher resolution obtainable. Such resolution was desirable since several of the films, notably that of purine itself (see Fig. 1) yielded numerous very sharp absorption peaks with a width of the order of 10 cm.$^{-1}$.

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

(9) R. K. Robins, K. L. Dille, C. H. Willits and B. E. Christensen, THIS JOURNAL, **75**, 263 (1953).

(10) A. Albert and D. J. Brown, *J. Chem. Soc.*, 2060 (1954).

(11) E. Vischer and E. Chargaff, *J. Biol. Chem.*, **168**, 781 (1947).

Conjugate Addition Reactions of Azoles. II. 1,2,4-Triazole, Tetrazole, Nitropyrazoles and Benzotriazole

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In a previous paper[1] we reported our observations on the conjugate addition of 1,2,3-triazole and benzotriazole to a variety of α,β-unsaturated carbonyl compounds. We have completed additional studies of this reaction in which 1,2,4-triazole, tetrazole, 4-nitropyrazole and 3,5-dimethyl-4-nitropyrazole have been added to acrylic acid, benzalacetophenone, benzalacetone, *p*-methoxybenzalacetophenone and dibenzalacetone, and in which benzotriazole has been added to *m*- and *p*-nitrobenzaldehyde. The addition reaction is carried out using an alkaline catalyst—either pyridine or Triton B—and the product is isolated from the reaction mixture in various ways dependent on the chemical properties and solubilities of the products. Some of the products are insoluble in both ether and water and can be separated from the reactants by washing with water to remove the azole and with ether to remove the unsaturated carbonyl compound. The unusual combination of water and carbon tetrachloride solubility of 1-phenyl-1-(1′-tetrazolyl)-butanone-3 is noteworthy.

The structures of the adducts obtained from the pyrazoles, from tetrazole and from 1,2,4-triazole can be assigned with reasonable certainty. Two principal problems are encountered. These involve the alternative structures which may result from 1,2- as opposed to 1,4-addition and the isomeric structures which result from reactions of the tetrazole and the triazole in tautomeric forms to give products substituted on one or the other of two nitrogen positions. Although 1,2-addition of azoles is entirely feasible, as is shown by the data recorded herewith on the 1,2-addition of benzotriazole to *m*- and *p*-nitrobenzaldehydes and as previously reported to cinnamaldehyde, the products obtained in these studies usually appear as 1,4-adducts whenever 1,4-addition is possible. The presence of the carboxylic acid group in the acrylic acid adducts from the pyrazoles, tetrazole and 1,2,4-triazole establish these as 1,4-adducts. The ultraviolet absorption data for products having a phenyl ketone structure show the customary carbonyl absorption again establishing 1,4-addition. For example, acetophenone has an absorption maximum at 245 mμ (log ϵ 4.0) and β-phenyl-β-(1′-tetrazolyl)-propiophenone has a maximum at 243 mμ (log ϵ 4.12).

There is a unique feature of structural significance in the ultraviolet absorption of the tetrazole adducts. A broad, intense absorption band in the 275–315 mμ range is shown by β-phenyl-β-(1′-tetrazolyl)-propiophenone (log ϵ 3.55 at 295–315 mμ); by 1-phenyl-1-(1′-tetrazolyl)-butanone-3 (log ϵ 3.60 at 275–295 mμ); and by 1,5-diphenyl-5-(1′-tetrazolyl)-1-pentenone-3 (log ϵ 4.4 at 285–305 mμ). Simple carbonyl compounds do not absorb in this region and even when conjugated with an aromatic ring as in acetophenone the absorption band in this range is much weaker (log ϵ 3.1 at 286 mμ) and is more narrow. It is possible that the carbonyl absorption in the two of these compounds in which the carbonyl group is thus conjugated may contribute to the absorption in this range—but the contribution cannot be very significant since the intensity of the absorption for the phenyl ketone is nearly the same as that of the methyl ketone. Furthermore, absorption in this range is strikingly absent from the spectra of the closely related 1-phenyl-1-[1′-(1,2,3-triazolyl)]-butanone-3. This absorption also may result from the phenyltetrazolylmethane structure. That such structural types might absorb in this region is suggested by the data for diphenylmethane[2] (log ϵ 2.7 at 262 mμ, with

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(1) R. H. Wiley, N. R. Smith, D. M. Johnson and J. Moffat, THIS JOURNAL, **76**, 4933 (1954).

(2) W. R. Orndorff, R. C. Gibbs, S. A. McNulty and C. B. Shapiro, *ibid.*, **49**, 151 (1927).

TABLE I

PREPARATION OF ADDUCTS

Starting materials[a]	Yield[b]	Recryst.[c] from	M.p., °C. corr.
1,2,4-Triazole (1.4); acrylic acid (1.44)	0.52, 19	W	175–178
1,2,4-Triazole (0.69); benzalacetophenone (2.08)	1.75, 63	CD	83–85
Tetrazole (1.4); acrylic acid (1.44)	0.60, 21	W	129–131
Tetrazole (1.4); dibenzalacetone (2.34)	0.35, 10	E	153–154
Tetrazole (0.7); benzalacetone (1.46)	1.1, 51	CT, W, or CL	85–86
Tetrazole (0.7); *p*-methoxybenzalacetone (1.76)	1.55, 63	CD or CT	105–106
Tetrazole (0.7); benzalacetophenone (2.08)	1.50, 54	M	105–106
4-Nitropyrazole (0.5); acrylic acid (0.4)	0.5, 60	To	132–135
3,5-Dimethyl-4-nitropyrazole (1.0); acrylic acid (0.6)	.6, 63	To	121
3,5-Dimethyl-4-nitropyrazole (0.2); benzalacetophenone (0.15)	.15, 31	E	124–126
Benzotriazole (1.5); *p*-nitrobenzaldehyde (1.0)	.25, 15	CT	101–102[d]
Benzotriazole (3.6); *m*-nitrobenzaldehyde (1.6)	.25, 7	CT	89–90

[a] Amounts of materials used are given in parentheses in grams. All were prepared by various modifications of techniques described in the previous article (reference 1) using Triton B as catalyst in all except the first listed for which pyridine was used as catalyst. [b] The first figure gives the gram yield, the second the percentage yield. [c] W, water; CD, carbon disulfide; E, ethanol; CT, carbon tetrachloride; CL, chloroform; M, methanol; To, toluene. [d] Mixed m.p. with benzotriazole and with *p*-nitrobenzaldehyde showed marked depressions.

TABLE II

ANALYTICAL DATA

Compound	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
β-[1′-(1,2,4-Triazolyl)]-propionic acid[a]	42.55	42.35	5.00	5.00		
β-Phenyl-β-[1′-(1,2,4-triazolyl)]-propiophenone	73.62	73.45	5.45	5.57	15.15	14.93
β-(1′-Tetrazolyl)-propionic acid[b]	33.80	33.78	4.26	4.05	39.43	39.18
1,5-Diphenyl-5-(1′-tetrazolyl)-1-pentenone-3	71.03	70.53	5.30	5.43	18.41	18.74
1-Phenyl-1-(1′-tetrazolyl)-butanone-3	61.09	61.03	5.59	5.56	25.91	26.18
1-(*p*-Methoxyphenyl)-1-(1′-tetrazolyl)-butanone-3	58.52	58.00	5.73	5.73	22.75	23.35
β-Phenyl-β-(1′-tetrazolyl)-propiophenone	69.05	69.02	5.07	4.90	20.13	20.26
β-[1′-(4′-Nitropyrazolyl)]-propionic acid[c]	38.92	39.04	3.81	3.81	22.70	22.56
β-[1′-(3′,5′-Dimethyl-4′-nitropyrazolyl)]-propionic acid[d]	45.07	44.83	5.20	5.05	19.71	19.68
β-(Phenyl β-[1′-(3′,5′-dimethyl-4′-nitropyrazolyl)]-propiophenone	68.75	68.78	5.48	5.50	12.03	11.90
1-Benzotriazolyl-4-nitrophenylcarbinol	57.77	57.96	3.73	3.93		
1-Benzotriazolyl-3-nitrophenylcarbinol	57.77	57.69	3.73	3.81	20.73	20.91

Neut. equiv.: [a] calcd., 141; found, 144. [b] Calcd. 142.1; found, 141.3. [c] Calcd., 185.1; found, 188.5. [d] Calcd., 213.2; found, 213.3.

less intense maxima at 254 and 271 mμ), but is entirely missing from the absorption data for the analogous 1,2,3-triazole structures previously reported. No chemical or physical method is at present available which will provide a basis for final assignment of structure based on the isomeric structures derived from tautomeric forms of the azoles. Pending development of such techniques and data, these compounds have been tentatively assigned the 1-tetrazolyl and 1-triazolyl structure which is commonly accepted for products obtained by N-substitution reactions.

Experimental

The 1,2,4-triazole used in the following experiments was prepared from formylhydrazine and formamide[3]; the tetrazole by deamination[4] of 5-aminotetrazole; the nitropyrazoles by nitration of pyrazole, prepared from hydrazine and tetraethoxypropane,[5,6] and of 3,5-dimethylpyrazole.[7] The other materials were obtained from commercial sources.[8] The data describing the preparations and the properties of the products are given in Tables I and II.[9]

Ultraviolet absorption spectra were determined in alcohol solutions using 1-cm. silica cells in a Beckman DU spectrophotometer.

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[3] G. Pellizarri, *Gazz. chim. ital.*, **24**, II, 222 (1894).

[4] R. A. Henry and W. B. Finnegan, THIS JOURNAL, **76**, 290 (1954).

[5] R. G. Jones, *ibid.*, **71**, 3994 (1949).

[6] The authors wish to thank the Carbide and Carbon Chemicals Corporation for supplying samples of tetraethoxypropane.

[7] R. H. Wiley and P. E. Hexner, *Org. Syntheses*, **31**, 43 (1951).

[8] The authors wish to thank the B. F. Goodrich Company for supplying samples of glacial acrylic acid.

[9] Carbon, hydrogen and nitrogen analyses by Micro-Tech. Laboratories, Skokie, Ill.