Preparation of Pyrazinoyldiazomethane and ω-Chloromethylpyrazinoyl Ketone

BY MORTON D. GLANTZ[1] AND PAUL E. SPOERRI

Pyrazinoic acid was prepared according to the method of Hall and Spoerri.[2]

Pyrazinoyl Chloride.[3]—Five-tenths (0.5) gram of pyrazinoic acid was treated with 10 ml. of thionyl chloride and the mixture, protected by a calcium chloride tube, was refluxed for two hours to give a clear purple solution. Evaporation of excess reagent gave a purple residue which was sublimed to yield colorless needles. The pyrazinoyl chloride thus formed turns somewhat yellow on exposure to air; m. p. with decomposition, 55–56°.

Pyrazinoyldiazomethane.—A dried ethereal solution of diazomethane[4] was cooled to 0–5°. To this was added, with continuous cooling and efficient stirring in small portions, freshly prepared pyrazinoyl chloride. A brisk evolution occurred as the acid chloride was added. The solution was allowed to stand overnight at room temperature, after which it was filtered and the ether removed under reduced pressure. A golden residue is thus formed. This was recrystallized several times from low-boiling petroleum ether; m. p. 85.5–86°.

A sample of the material was tested with a few drops of concentrated hydrochloric acid. A vigorous evolution of nitrogen took place.

Anal. Calcd. for $C_6H_4ON_4$: C, 48.65; H, 2.72. Found: C, 48.14; H, 2.77. Side-chain nitrogen calcd., 18.92. Found: 18.63.

ω-Chloromethylpyrazinoyl Ketone.—A solution of pyrazinoyldiazomethane in anhydrous ether was treated with gaseous anhydrous hydrogen chloride until no further nitrogen was evolved. The white suspension was boiled gently to remove the excess hydrogen chloride and then extracted with hot low-boiling petroleum ether and allowed to crystallize; m. p. 89–89.5°.

Anal. Calcd. for $C_6H_5ON_2Cl$: C, 46.02; H, 3.22. Found: C, 45.85; H, 3.09.

The Wolff[5] rearrangement on the pyrazinoyldiazomethane did not prove successful.

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(1) Department of Chemistry, Brooklyn College, Brooklyn, N. Y.

(2) Hall and Spoerri, THIS JOURNAL, **62**, 664 (1940).

(3) Meltzner, Thesis, Polytechnic Institute of Brooklyn, 1949.

(4) Arndt, *Org. Syntheses*, **15**, 4 (1935).

(5) Wolff, *Ann.*, **394**, 25 (1912).

DEPARTMENT OF CHEMISTRY
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Alanine, Glycine and Proline Contents of Casein and its Components[1]

BY WILLIAM G. GORDON, WILLIAM F. SEMMETT AND MAURICE BENDER

In a previous paper[2] on the amino acid composition of casein, α-casein and β-casein, alanine analyses were listed as provisional. We wish now to record results of more accurate alanine determinations as well as revised figures for glycine and proline. The present analyses were made by the radioisotope derivative technique of Keston, Udenfriend and Cannan,[3] a method both highly specific and accurate. γ-Casein, a third component of casein, recently isolated in this laboratory[4] has also been analyzed for these amino acids. Average results (corrected for moisture and true ash) of triplicate analyses, shown in the table are believed to be more accurate than our previously published figures. The values for whole casein are now in closer agreement with reliable figures in the literature (alanine, 3.5%[5]; glycine, 1.9%[6]; and proline, 10.5%[7]).

	Alanine	Glycine	Proline
	G./100 g. protein		
Whole casein	3.20	2.00	10.6
α-Casein	3.81	2.26	7.47
β-Casein	1.99	1.56	15.1
γ-Casein	2.29	1.48	17.0

The radioisotope derivative technique was used also for determination of hydroxyproline in protein hydrolyzates according to the method of Keston,[8] *et al.*, and showed that whole casein contains less than 0.1% of this amino acid.

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(1) These analyses are included in a thesis submitted by M. Bender to the Graduate School of Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Article not copyrighted.

(2) Gordon, Semmett, Cable and Morris, THIS JOURNAL, **71**, 3293 (1949).

(3) (a) Keston, Udenfriend and Cannan, *ibid.*, **71**, 249 (1949). (b) The I^{131} used in this investigation was supplied by Carbide and Carbon Chemicals Corp., Oak Ridge National Laboratory, on allocation from the Isotopes Division, U. S. Atomic Energy Commission.

(4) Hipp, Groves, Custer and McMeekin, Am. Chem. Soc., Philadelphia meeting, April, 1950.

(5) Tristram, *Biochem. J.*, **40**, 721 (1946).

(6) Shankman, Camien and Dunn, *J. Biol. Chem.*, **168**, 51 (1947).

(7) Dunn, McClure and Merrifield, *ibid.*, **179**, 11 (1949).

(8) Keston, Udenfriend, Levy and Cannan, personal communication.

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Dichlorodiphenyltrichloroethane. II. Analogs. *p,p'*-DFDT and its Degradation Products[1]

BY F. A. GUNTHER AND R. C. BLINN

Bradlow and VanderWerf[2] have reported the only available systematic study of the preparation and chemical composition of the insecticidal material 2,2-bis-(*p*-fluorophenyl)-1,1,1-trichloroethane (*p,p'*-DFDT). Despite its expensive synthesis when carried out in the usual manner, the fact that this compound has consistently been superior to 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane (*p,p'*-DDT) when tested repeatedly against a number of species of insects in our own laboratories[3] has warranted the continuation of the investigation of this compound, begun in 1946. Because the mechanism(s) of action of the DDT-

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(1) Paper No. 642, University of California Citrus Experiment Station, Riverside, California. Presented before the Division of Organic Chemistry of the American Chemical Society, San Francisco, March, 1949.

(2) Bradlow and VanderWerf, THIS JOURNAL, **69**, 662 (1947); *cf.* Iris and Mendizabal, *Rev. inst. salubridad y enfermedad. trop.*, **8**, 63 (1947); *Chem. Abstracts*, **42**, 1920i (1948).

(3) Metcalf, *J. Econ. Entomol.*, **41**, 416 (1948).