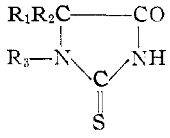
School showed 5-phenyl-2-thiohydantoin, 5-(p-hydroxybenzyl)-2-thiohydantoin and the compounds described here to have no activity against several vaccinia strains.

We are reporting the synthesis of nine new thiohydantoins which are listed in Table I. The amino acids used were commercially available or easily prepared by standard methods with the exception of the 5-(2- and 3-thenyl)-thiohydantoins where the acetylated amino acids were employed. Deacetylation was acccomplished by refluxing the 1-acetyl-5-substituted thiohydantoin for one to two hours in sufficient 10% hydrochloric acid to obtain solution of the thiohydantoin. Deacetylation of 1-acetyl-5-(β-ethylmercaptoethyl)-2-thiohydantoin was accomplished without isolation of the solid acetyl intermediate.

TABLE I

5-SUBSTITUTED THIOHYDANTOINS



R₁	R₃	M.p., °C.[a]	Yield, %[b]	Nitrogen,[c] % Calcd.	Nitrogen,[c] % Found
C_6H_5–[d]	CH_3CO	173.5–174[e]	36	11.28	11.50
p-ClC_6H_4–	CH_3CO	167–168[e]	71	9.91	10.23
p-BrC_6H_4–	CH_3CO	188–188.5[e]	65	8.56	8.46
$C_2H_5SCH_2CH_2$–	CH_3CO	58–58.5[f]	69	11.38	11.21
$C_2H_5SCH_2CH_2$–	H	99.5–100.5[g]	69	13.71	13.44
3-C_4H_3S–[h]	CH_3CO	157–158[e]	75	11.02	11.00
3-C_4H_3S–	H	177–178[g]	82	13.20	13.28
2-C_4H_3S–	CH_3CO	167–168[e]	92	11.02	11.15
2-C_4H_3S	H	197–198(dec.)[g]	93	13.20	13.09

[a] All melting points uncorrected, Fisher–Johns block. [b] Based on crude yields, the melting point of which is within 4° of that reported. [c] All analyses by Miss J. W. Dickey. [d] R_2 is methyl in this compound, H in all others. [e] Recrystallized from ethanol–water. [f] Recrystallized by slow evaporation of ethanol solution. [g] Recrystallized from water. [h] Originally synthesized by R. L. Hardin in this Laboratory.

Undoubtedly higher yields of some of the thiohydantoins could be realized if crude oily products were not sometimes encountered in the isolation. It was observed that prolonged mechanical stirring of an oily or semi-solid product in a water solution at ice-bath temperatures gave a better crystalline product. The thiohydantoins were finally recrystallized by dissolving in excess alcohol at room temperature and slowly adding water until saturation was reached, or by concentration under an air jet. Heating or extreme cooling of the recrystallizing medium led to various amounts of oily products.

Experimental

2-Thenylacetamidomalonic Acid.—Saponification of 7.7 g. (0.025 mole) of diethyl 2-thenylacetamidomalonate[6] with 25 ml. of 10% sodium hydroxide gave 5.9 g. (93.5%) of 2-thenylacetamidomalonic acid, which melted with evolution of carbon dioxide at 128.5–129°.

Anal. Calcd. for $C_{10}H_{11}O_5NS$: C, 46.70; H, 4.31. Found: C, 47.10; H, 4.49.

N-Acetyl-β-2-thienylalanine.—Decarboxylation was carried out on 5.6 g. (0.0218 mole) of 2-thenylacetamidomalonic acid in 50 ml. of water to give 4.0 g. (86%) of N-acetyl-β-2-thienylalanine, m.p. 128–129°.[7] A mixture of a sample of this compound with 2-thenylacetamidomalonic acid gave a depressed melting range.

1-Acetyl-5-(2-thenyl)-2-thiohydantoin.—The following procedure is typical of the thiohydantoin preparations. A solution of 4.0 g. (0.0188 mole) of N-acetyl-β-2-thienylalanine and 1.9 g. (0.025 mole) of ammonium thiocyanate in 5 ml. of glacial acetic acid and 25 ml. of acetic anhydride was refluxed on a steam-bath for one hour. The cooled solution was then added to 200 ml. of water with mechanical stirring to give 4.4 g. (92%) of cream colored crystals, m.p. 164–166°. Recrystallization from aqueous ethanol raised the melting point to 167–168°.

5-(2-Thenyl)-2-thiohydantoin.—A solution of 0.5 g. (0.002 mole) of 1-acetyl-5-(2-thenyl)-2-thiohydantoin in 25 ml. of 10% hydrochloric acid was refluxed for one hour, and then chilled to give 0.39 g. (93.5%) of 5-(2-thenyl)-2-thiohydantoin, which melted at 197–198° with decomposition after recrystallization from water.

5-(3-Thenyl)-2-thiohydantoin.—1-Acetyl-5-(3-thenyl)-2-thiohydantoin was prepared in an identical manner from N-acetyl-β-3-thienylalanine,[8] and readily deacetylated as above to yield white needles, melting at 177–178°.

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[6] K. Dittmer, W. Herz and J. S. Chambers, *J. Biol. Chem.*, **166**, 541 (1946).

[7] K. Dittmer, *et al.*, THIS JOURNAL, **71**, 1202 (1949), reports the m.p. to be 130°.

[8] R. G. Garst, E. Campaigne and H. G. Day, *J. Biol. Chem.*, **180**, 1016 (1949).

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The Fluoroplatinates. II. Fluoroplatinic Acid

BY ROY S. CLARKE, JR.,[1] AND THEODORE P. PERROS

RECEIVED JUNE 22, 1953

The first paper in this series dealt with the preparation and properties of certain rare earth fluoroplatinates.[2] Prior to this, the only compounds containing the fluoroplatinate ion were certain ones from the alkali group elements.[3–5]

This paper is to report the preparation and isolation of fluoroplatinic acid.

Experimental

Fluoroplatinic Acid.—Lanthanum fluoroplatinate was prepared as previously described.[2] About 60 ml. of a 0.04 M solution of this salt was passed through an ion-exchange column at a rate of 3–4 ml. per minute. The dimensions of the column were 3.5 × 90 cm. and it was packed with 40–60 mesh Dowex-50 resin. The resin was hydrogen charged prior to the introduction of the salt solution.

The column was eluted with water at a rate of 3–4 ml. per minute. The yellow color of the fluoroplatinate ion appeared shortly after a liter of water had passed through the column. The elution process required less than two liters for its completion. The solution was stored in a polyethylene bottle. Tests for the lanthanum ion on this solution were negative.

A portion of this solution was evaporated to dryness in a polyethylene beaker by vacuum desiccation over sodium hydroxide pellets. Yellow crystals of hydrated fluoroplatinic acid were obtained.

This acid is hygroscopic and very soluble in water. The addition of a potassium salt to a solution of this acid precipitated the yellow crystalline potassium fluoroplatinate. The characteristic color of the iodoplatinate ion appeared slowly when iodide ion was added to the acid. Hydrogen was liberated when zinc was added to the acid.

Absorption Spectrum.—The absorption spectrum of the fluoroplatinic acid was measured with a Model DU Beckman spectrophotometer using matched 1-cm. cells. The curve was identical to that previously reported for the fluoroplatinate ion, having maxima at 275 and 318 mμ (not at

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[1] Abstracted from a portion of the thesis to be submitted by Roy S. Clarke, Jr., in partial fulfillment of the requirements for the degree of Master of Arts.

[2] T. P. Perros and C. R. Naeser, THIS JOURNAL, **75**, 2516 (1953).

[3] H. Schlesinger and M. Tapley, *ibid.*, **46**, 276 (1924).

[4] A. G. Sharpe, *J. Chem. Soc.*, 3444 (1950).

[5] A. G. Sharpe, *ibid.*, 197 (1953).

308 mμ as erroneously printed in the first paper of this series).

Analyses.—Aliquot portions of a stock solution of fluoroplatinic acid were titrated with 0.0219 *N* sodium hydroxide. The course of the reaction was followed with a Model G Beckman *p*H meter. The titation curve was typical of the reaction between a strong base and a strong acid.

Aliquot portions of the same stock solution were analyzed for platinum content by reduction of the acid with hydrazine. The results confirmed the existence of the dibasic fluoroplatinic acid.

Acknowledgment.—Part of this investigation was performed under the terms of a contract with the AEC, Washington, D. C.

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Some Solvent and Salt Effects in the Solvolysis of *s*-Butyl Bromide[1]

BY W. C. COBURN, JR., ERNEST GRUNWALD AND HENRY P. MARSHALL

RECEIVED JULY 10, 1953

The solvolysis of *s*-alkyl halides proceeds by a mechanism which cannot be classified as either S_N1 or S_N2.[2,3] On the one hand, there is stereochemical evidence of partial racemization in the solvolysis of 2-bromoöctane[4] and probably of *s*-butyl *p*-toluenesulfonate,[5] suggesting the existence of a metastable solvolysis intermediate. On the other hand, there is kinetic evidence for isopropyl bromide which indicates the nucleophilic participation of solvent in systems such as ethanol–water.[2]

We now wish to report some rate studies on the solvolysis of *s*-butyl bromide, a representative member of this interesting group of reagents. First-order rate constants have been measured in a number of solvents, including acetic acid, ethanol and ethanol–water mixtures, and are equal, within a few per cent., to the corresponding rate constants for isopropyl bromide. The results are shown in Table I. Without repeating the analysis of rate constants which was made previously for isopropyl bromide,[2] we may therefore conclude that there is nucleophilic participation of solvent in the solvolysis of *s*-butyl bromide in systems such as ethanol–water.

TABLE I

COMPARISON OF SOLVOLYSIS RATE CONSTANTS FOR ISOPROPYL AND *s*-BUTYL BROMIDE

Solvent	Temp., °C.	$10^6 k$ (sec.$^{-1}$) for Isopropyl bromide	*s*-Butyl bromide
Abs. EtOH[a]	50.0	0.112	0.098
80 Vol. % EtOH[a]	50.0	1.18	1.06
60 Vol. % EtOH[b]	80.0	70.6	74.1
Glacial HOAc	100.0	0.89	0.96

[a] Data for isopropyl bromide in abs. and 80% EtOH were taken from ref. 2. [b] M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948).

We also tried to obtain evidence for a metastable reaction intermediate by looking for a mass-law effect.[6] The pertinent data in 75.00 wt. % ethanol–water at 50° are shown in Table II. The Table lists the rate constants for solvolysis in the presence of varying concentrations of salt for sodium bromide, a common ion salt,[6] and for sodium perchlorate and sodium *p*-toluenesulfonate, two unreactive "neutral" salts. The rate constants are generally based on at least two rate runs, and their probable errors are about 1.6%. If, to a first approximation, the neutral salt effects are treated as colligative functions of the ionic strength, the rate constants at a given salt concentration should be equal for the two neutral salts, and possible decreases below this value due to sodium bromide should measure the magnitude of the mass-law effect. As is shown in the table, the rate constants at a given ionic strength are indeed approximately equal for the neutral salts, but are greater rather than less in the presence of sodium bromide. Thus there is no evidence for a mass-law effect.

TABLE II

EFFECT OF ADDED SALTS ON THE SOLVOLYSIS RATE OF *s*-BUTYL BROMIDE IN AQUEOUS ETHANOL, 75.00 WEIGHT % ETHANOL,[a] 50.00 ± 0.02°

Salt	*M*	$10^6 k$ (sec.$^{-1}$)[b]	Salt	*M*	$10^6 k$ (sec.$^{-1}$)[b]
None	..	1.06	$NaClO_4$	0.18	1.09
NaBr	0.20	1.20		.45	1.0
	.50	1.17		.80	1.09
	.77	1.19	NaOTs	.21	1.08
				.43	1.04

[a] 79.22 vol. %. [b] Probable errors in *k*: 0.45 *M* $NaClO_4$, 4%; all other values, 1.6%.

Within the limits of present knowledge, this conclusion cannot be reversed if the salt effects are treated as specific rather than colligative. In aqueous solution salt effects on non-electrolytes often parallel either the salt polarizability or the electrostriction of the solvent due to the electrolyte.[7] The relevant values of the apparent molar refractions, *R*, and of ($\bar{V}_s^\circ - V_s$) are summarized in Table III. The values are apparently not very sensitive to change in solvent from water to 75.00% ethanol, as is illustrated for sodium *p*-toluenesulfonate. It is seen that, on the basis of the molar refractions, the neutral salt effects ought to be nearly equal for sodium bromide and sodium perchlorate but ought

TABLE III

Salt	Solvent	$(\bar{V}_s^\circ - V_s)$[a]	*R*
NaBr	HOH	−10.5[b]	12.78[d], 12.8[c]
$NaClO_4$	HOH	− 7.5[b]	13.32[d]
NaOTs	HOH	−10[c]	43.4[c]
	75.00% Ethanol	−7[c]	43.2[c]

[a] $\bar{V}_s^\circ$ = partial molar volume of salt in very dilute solution. V_s = molar volume of (metastable) pure liquid salt. [b] Taken from W. F. McDevit and F. A. Long, THIS JOURNAL, **74**, 1773 (1952). [c] Own measurements at 25.44°. For V_s use molar volume of crystalline solid salt. (See B. Lunden, *Z. physik. Chem.*, 192, 345 (1943).) [d] Taken from K. Fajans and G. Joos, *Z. Physik*, **23**, 1 (1924).

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(1) Supported in part by the Research Corporation and by the Office of Ordnance Research, U. S. Army.

(2) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

(4) E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 1196 (1937).

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(6) (a) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 979 (1940); (b) O. T. Benfey, E. D. Hughes and C. K. Ingold, *ibid.*, 2488 (1952).

(7) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).