Lord, Jr., and D. H. R. Barton gave valuable advice for the theoretical part.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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Organic Salts of Benzylpenicillin. I. Aliphatic Amine Vasoconstrictors

BY H. W. RHODEHAMEL, JR.

During the preparation of a series of organic amine salts of benzylpenicillin, a number of crystalline combinations have been found. This note deals with the relatively water soluble crystalline benzylpenicillin salts of three useful aliphatic amine vasoconstrictors which have been of sufficient interest to suggest possible clinical application. Each is prepared in the same manner as follows: The free amine base in a convenient organic solvent, generally amyl acetate or diethyl ether, is added to an organic solution of free benzylpenicillin acid. The salt combination precipitates out as crystals immediately or after short standing with scratching or seeding.

The 2-Aminoheptane Salt of Benzylpenicillin.—White, needle-like crystals with a theoretical penicillin potency of 1270 Oxford units per mg.; m.p. (hot stage) 102–105° dec.; $[\alpha]^{25}\text{D} + 225 \pm 3°$ (c, 1 in H_2O). *Anal.* Calcd. for $C_{23}H_{35}O_4N_3S{\cdot}H_2O$: C, 59.09; H, 7.98; N, 8.99. Found: C, 59.99; H, 8.56; N, 8.89.

The 2-Amino-4-methylhexane Salt of Benzylpenicillin.—White, small, needle-like crystals with a theoretical penicillin potency of 1270 Oxford units per mg., m.p. (hot stage) 103–106° dec.; $[\alpha]^{25}\text{D} + 225 \pm 3°$ (c, 1 in H_2O). *Anal.* Calcd. for $C_{23}H_{35}O_4N_3S{\cdot}H_2O$: C, 59.09; H, 7.98; N, 8.99. Found C, 59.00; H, 7.87; N, 8.94.

The 1-Cyclopentyl-2-methylaminopropane Salt of Benzylpenicillin.—White, needle-like crystals with a theoretical penicillin potency of 1200 Oxford units per mg., m.p. (hot stage) 202–204° dec. *Anal.* Calcd. for $C_{25}H_{37}N_3O_4S{\cdot}H_2O$: C, 60.70; H, 8.15; N, 8.50. Found: (ash free) C, 61.21; H, 6.36; N, 8.86.

Another commerically available aliphatic amine vasoconstrictor, 1-cyclohexyl-2-methylaminopropane, has given a water soluble, amorphous salt with benzylpenicillin, but efforts to induce its crystallization have to date been unsuccessful.

The author is indebted to Mr. W. L. Brown for microanalyses, to Dr. E. Rohrmann for supplying the amines used in this study, and to Miss Mary Stieff for technical assistance.

THE LILLY RESEARCH LABORATORIES
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The Trimer of *o*-Phthalonitrile[1]

BY SIDNEY D. ROSS AND MORTON FINEMAN

In the course of their work on magnesium phthalocyanine, Linstead and Lowe[2] isolated an acetic acid soluble by-product melting at 296° and analyzing correctly for a polymer of phthalonitrile, $(C_8H_4N_2)_x$. In a later publication Dent and Linstead[3] showed by a molecular weight determination that this substance was a trimer, and that on hydrolysis with nitric acid it yielded phthalimide. On the basis of this evidence they assigned to the trimer a 2,4,6-tri-(*o*-cyanophenyl)-1,3,5-triazene structure. It is the purpose of the present communication to report a preparation of this trimer, some of its properties, and evidence confirming Linstead's structure assignment.

In connection with other work in these laboratories, we have observed that when *o*-phthalonitrile is heated at high temperature in the presence of a trace of acid or water, the trimer, reported by Linstead and Lowe, is formed. The trimer gives a yellow solution in sulfuric acid, from which phthalimide can be isolated after dilution with water.

The Linstead structure was confirmed by comparing the infrared spectrogram[4] of the trimer, mulled in nujol, with that of 2,4,6-triphenyl-1,3,5-triazene prepared by the method of Cook and Jones.[5] The *o*-phthalonitrile trimer (Figs. 1 and 2) shows the expected nitrile absorption at 4.53 microns, and the other absorptions can be attributed to the benzene ring, the triazene ring or the nujol vehicle. The spectrum of 2,4,6-triphenyl-1,3,5-triazene (Fig. 3) is shown for comparison.

All of the *o*-phthalonitrile trimer samples which we prepared were crystallized from acetic acid. Nevertheless, we observed that we obtained the product in two crystalline modifications, fine needles (Form A) and poorly defined clusters (Form B). Both crystalline forms melted at the same point and gave similar infrared spectrograms (Figs. 1 and 2). However, the two forms

TABLE I

X-RAY DIFFRACTION LINES FOR 2,4,6-TRI-(*o*-CYANOPHENYL)-1,3,5-TRIAZENE (FORM A)

#[a]	θ[b]	d[c]	I[d]
1	4.35	10.1	V. S.
2	5.90	7.49	M
3	7.10	6.25	S
4	8.96	4.94	M
5	11.30	3.92	S
6	12.7	3.50	S
7	13.5	3.30	V. S.
8	15.0	2.96	W
9	16.0	2.79	W
10	17.5	2.56	W
11	18.9	2.38	W
12	20.9	2.16	W
13	22.0	2.05	W
14	22.8	1.98	W
15	23.5	1.93	W
16	26.6	1.72	W
17	27.8	1.65	W

TABLE II

X-RAY DIFFRACTION LINES FOR 2,4,6-TRI-(*o*-CYANOPHENYL)-1,3,5-TRIAZENE (FORM B)

#	θ	d	I
1	4.14	10.7	V. S.
2	6.38	6.92	W
3	7.68	5.75	M
4	9.12	4.85	W
5	9.87	4.49	W
6	10.6	4.19	W
7	11.4	3.89	V. W.
8	12.0	3.70	W
9	13.6	3.27	V. S.
10	14.6	3.05	W
11	21.6	2.09	W
12	27.7	1.65	W

[a] #, order in which lines found. [b] θ, Bragg angl. [c] *d*, interplanar spacing. [d] *I*, qualitative intensity.

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[1] This work was performed under contract no. W36-039-sc-38142 with the Signal Corps of the United States Army.

[2] R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, 1022 (1934).

[3] C. E. Dent and R. P. Linstead, *ibid.*, 715 (1938).

[4] The spectra were determined by Philip Sadtler of Samuel P. Sadtler and Son, Inc.

[5] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

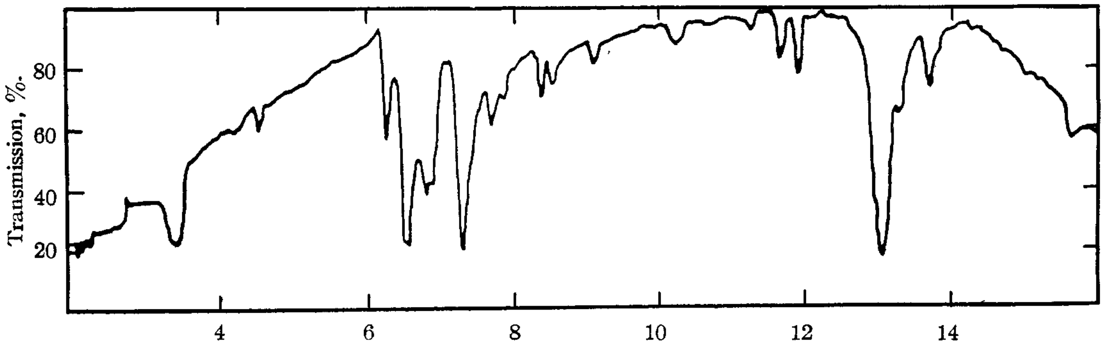

Fig. 1.—Infrared spectrogram of 2,4,6-tri-(*o*-cyanophenyl)-1,3,5-triazene (Form A).

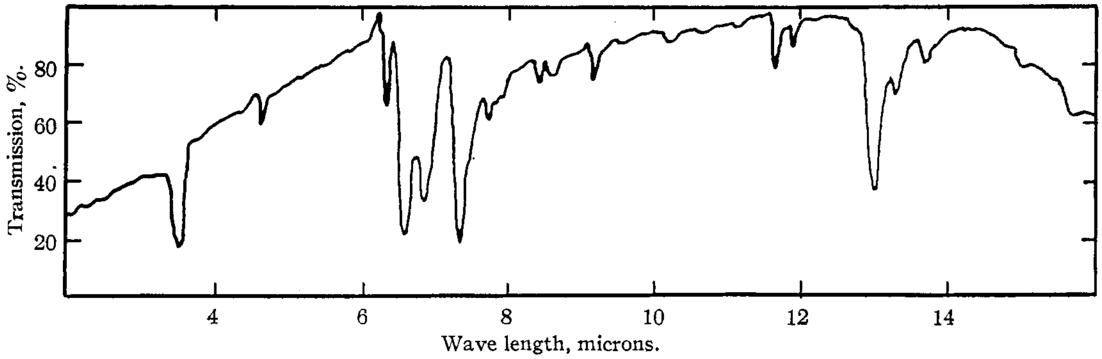

Fig. 2.—Infrared spectrogram of 2,4,6-tri-(*o*-cyanophenyl)-1,3,5-triazene (Form B).

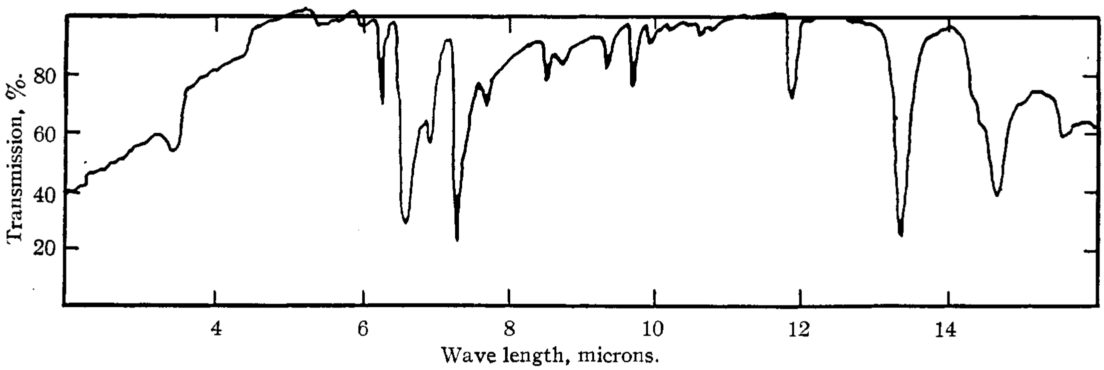

Fig. 3.—Infrared spectrogram of 2,4,6-triphenyl-1,3,5-triazene.

gave distinctly different X-ray diffraction patterns. The lines for Form A are presented in Table I and Form B in Table II. When Form A was melted and resolidified, Form B was obtained, and Form A could not be obtained from Form B even by seeding with Form A. When Form A was held below its melting point at 275° it was partially converted into Form B. We, therefore, conclude that the B form is the stable one.

Experimental[6]

2,4,6-Tri-(*o*-cyanophenyl)-1,3,5-triazene.—*o*-Phthalonitrile (10 g.) and water (0.1 g.) in a tube were immersed in a Dry Ice-bath, evacuated, sealed and, finally, heated at 325° for twenty hours. The crude product was extracted with water in a Soxhlet apparatus for 24 hours. The extract yielded 1 g. of phthalonitrile. The residue was dried and extracted in a Soxhlet apparatus with acetic acid. Evaporation of the acetic acid from the extract gave the crude trimer; yield, after two crystallizations from acetic acid, 4.5 g. (45%); m. p. 301.5–303°.

Anal. Calcd. for $(C_8H_4N_2)_x$: C, 75.00; H, 3.15; N, 21.87. Found: for Form A: C, 74.58, 74.69; H, 3.07, 3.01; N, 22.26, 22.34; for Form B: C, 75.36, 75.49; H, 3.33, 3.46; N, 20.67, 20.49.

The trimer (0.5 g.) was dissolved in concentrated sulfuric acid and permitted to stand 20 hours at room temperature. The solution was poured onto ice. The product was extracted with benzene, the benzene was removed, and the crude phthalimide was crystallized from acetone–water; yield, quantitative; m. p. 233–234°.

Anal. Calcd. for $C_8H_5O_2N$: N, 9.52. Found: N, 9.68, 9.53.

The X-ray diffraction diagrams were obtained on a

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(6) All analyses are by Dr. Carl Tiedcke.

North American Philips Company X-ray machine. The pictures were taken at 32 kilovolts and 22 milliamperes from a copper target using a nickel filter. The exposure periods were varied from one to five hours until good pictures were obtained.

CONTRIBUTION FROM THE
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Rhenium Iodide and Chloride

BY CHARLES L. RULFS AND PHILIP J. ELVING[1]

Noddack and Noddack[2] reported the formation of ReI_4 by the action of iodine vapor on rhenium metal. No confirmation of this compound could be found.[3] Since no simple iodides of rhenium are known, it was felt worthwhile to attempt the preparation of rhenium iodide by several different methods. In no case could any evidence of reaction be found. The methods tried include the following: (1) Rhenium powder was heated with iodine in a sealed tube for six hours at 170–180°. (2) Rhenium powder suspended in carbon tetrachloride containing an excess of dissolved iodine was refluxed for seventy-two hours.

Rhenium trichloride was prepared in poor yield by an adaptation of the Ruff synthesis[4] for iodine trichloride and monochloride.

Rhenium powder plus sulfuryl chloride, with and without traces of aluminum chloride present, were treated (a) by boiling for forty-eight hours at atmospheric pressure, (b) by heating in a sealed tube at 150° for six hours, and (c) by refluxing in excess ether for sixty hours. In every case a limited amount of reaction took place, the amount of which did not seem to be notably improved by longer treatment. Ether extraction of the reaction residues gave a red to violet solution which was filtered to remove unreacted rhenium. Vacuum evaporation of the ether left a red residue which had a high tendency to sublime or distil into the trap as a greenish vapor. Apparently, rhenium trichloride was the product of the reactions but the yield was poor under all conditions that were tried.

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[1] The Pennsylvania State College, State College, Penna.

[2] I. Noddack and W. Noddack, "Das Rhenium," Voss, Leipzig, 1933.

[3] J. G. F. Druce, "Rhenium," Cambridge Univ. Press, Cambridge, 1948.

[4] O. Ruff, *Ber.*, **34**, 1749 (1901).

DEPARTMENT OF CHEMISTRY
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LAFAYETTE, INDIANA RECEIVED AUGUST 6, 1949

Solubility of Thallous Rhenide[1a]

BY CHARLES L. RULFS[1b] AND PHILIP J. ELVING[1c]

The many apparent analogies of rhenide ion with the halides suggests the possible isolation of insoluble silver, lead or mercurous rhenide by precipitation. The powerful reducing action of rhenide ion, however, precludes these particular possibilities. Thallous ion, on the other hand, is not reduced by rhenide and the thallous halides are relatively insoluble.

Rhenide solution, 1 m*M* in rhenium and 2.4 *N* in hydrochloric acid, was prepared by zinc reduction under nitrogen in a water-cooled reductor as described by Lundell and Knowles.[2] The solution was saturated with thallous chloride at *ca.* 25° and then allowed to stand under nitrogen for ninety minutes at *ca.* 0°. The white crystals which separated from the test solution were examined microscopically and found to be isomorphous with thallous chloride. A portion of the washed precipitate was warmed and dissolved in bismuth trichloride solution, giving no evidence of any discoloration. A drop of the supernatant test solution gave an immediate black precipitate when added to the same tube, indicating the presence of rhenide in the supernatant liquid.

Contrary to expectation, it must be concluded from the failure of the compound to precipitate that thallous rhenide is considerably more soluble than is thallous iodide and at least twice as soluble as is the bromide. More specifically, the solubility of thallous rhenide (estimated from the known rhenide concentration in the presence of excess thallous ion) must be equal to or greater than 39 mg. per 100 ml. of 2.4 *N* hydrochloric acid at 0°. The solubilities[3] of the thallous halides in mg. per 100 ml. of water at 0° are: TlCl, 161; TlBr, 22; TlI, 2.

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[1] (a) The work described was performed while C. L. R. was the holder of an Atomic Energy Commission Predoctoral Fellowship. (b) University of Michigan, Ann Arbor, Mich. (c) The Pennsylvania State College, State College, Pa.

[2] Lundell and Knowles, *J. Research Nat. Bur Standards*, **18**, 629 (1937).

[3] A. Seidell, "Solubilities of Inorganic Compounds," ed. 3, D. Van Nostrand Co., New York, N. Y., 1940, pp. 1538 ff.

PURDUE UNIVERSITY AND
PURDUE RESEARCH FOUNDATION
LAFAYETTE, INDIANA RECEIVED AUGUST 6, 1949

Some Physical Constants of α-Tocopherylhydroquinone[1]

BY HARRIS ROSENKRANTZ AND A. T. MILHORAT

Recent reports from this Laboratory have demonstrated that α-tocopherylhydroquinone has vitamin E activity.[2,3] Since other workers undoubtedly will study this compound, a report on certain of its physical constants appears to be desirable. The substance may exist either as a waxy solid[4] or an oil at room temperatures. Fieser, Tishler and Wendler[5] prepared 2,3,5-trimethyl-6-phytyl-1,4-benzohydroquinone in crystalline form, and Tishler and Wendler[4] obtained tocopherylhydroquinone as a white waxy solid. We have succeeded in crystallizing tocopherylhydroquinone as short thin needles. Solutions containing 250 mg. α-tocopherylhydroquinone per cc. of absolute ethanol were placed in a desiccator immediately after hydrogenation and removal of the catalyst. The desiccator was evacuated at the water-pump for twenty-four hours; after the solution had stood for an additional period of twenty-four

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[1] Aided by the Armour Fund for Research in Muscular Disease and by a grant from The Nutrition Foundation, Inc.

[2] Ulick and Milhorat, *Science*, **110**, 531 (1949).

[3] Milhorat, Mackenzie, Ulick, Rosenkrantz and Bartels, *Annals N. Y. Acad. Sci.*, **52**, Art. 3, 334 (1949).

[4] Tishler and Wendler, THIS JOURNAL, **63**, 1532 (1941).

[5] Fieser, Tishler and Wendler, *ibid.*, **62**, 2865 (1940).