iodopropionate in ether. Upon distillation, it undergoes violent decomposition. For this investigation the ester was prepared in 78% yield from sodio-diethyl phosphite with ethyl β-bromopropionate in dry xylene. The product distilled very smoothly. The C-amide was obtained in the usual manner. The reactions may be summarized as follows

$$(C_2H_5O)_2OPNa + BrCH_2CH_2COOC_2H_5 \longrightarrow$$
$$(C_2H_5O)_2OPCH_2CH_2COOC_2H_5 \longrightarrow$$
$$(C_2H_5O)_2OPCH_2CH_2 \cdot CONH_2 \longrightarrow$$
$$(C_2H_5O)_2OPCH_2CH_2NH_2 \longrightarrow$$
$$(HO)_2OPCH_2CH_2NH_2HCl \longrightarrow (HO)_2OPCH_2CH_2NH_2$$

The amino acid is a colorless, crystalline substance freely soluble in water and insoluble in alcohol. It is stable to hot hydrochloric acid and possesses a characteristic titration curve with one sharp break, at *p*H 7.5, due to the zwitterion effect.

Experimental

β-Phosphonopropionic Acid Triethyl Ester.—To 68 g. of dry sodium ethoxide in 500 cc. of dry xylene, 138 g. of diethyl phosphite[3] is added slowly while stirring. When completely reacted, 181 g. of ethyl β-bromopropionate is added dropwise with vigorous stirring while the reaction mixture is kept in an ice–salt bath. After permitting the mixture to stand overnight to reach room temperature, it is warmed for two hours in a water-bath. After cooling, the sodium bromide is removed by filtering, the xylene distilled off *in vacuo* and the residual oil fractionated *in vacuo;* b. p. 141–143° at 9 mm. The ester is a clear, colorless liquid; yield, 78%.

β-Aminoethanephosphonic Acid.—To a solution of 30.8 g. of potassium hydroxide and 8 g. of bromine in 200 cc. of water at 0°, 10.45 g. of β-carbamylethanephosphonic acid diethyl ester is added and the mixture stirred until complete solution has occurred. After allowing the solution to stand overnight, at room temperature, 90 cc. of 48% hydrobromic acid is added when about one liter of carbon dioxide is evolved. The solution is evaporated to dryness *in vacuo* from a warm water-bath. The residue is treated with 75 cc. of water and filtered. The filtrate, at about *p*H 1, is heated in a sealed tube at 150–190° for two hours. The reaction mixture is then evaporated to dryness *in vacuo*, the residual cake extracted with 100 cc. of warm alcohol and the extract filtered. The filtrate is treated with excess aniline while stirring to precipitate the amino acid. After two recrystallizations from 50% alcohol, the product is pure; m. p. 281–282° (cor.), yield, 71%.

Anal. Calcd. for $C_2H_8NPO_3$: C, 19.20; H, 6.45; N, 11.20. Found: C, 19.21; H, 6.51; N, 10.55.

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[3] Milobendzki and Sachnowski, *C. A.*, **13**, 2865 (1919).

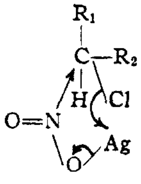
SCIENTIFIC DEPARTMENT
HOFFMANN-LA ROCHE, INC.
NUTLEY, N. J.

RECEIVED JULY 17, 1946

Reaction of *d*-α-Phenethyl Chloride with Silver Nitrite

BY RICHARD H. EASTMAN AND SIDNEY D. ROSS

The reaction of silver nitrite with optically active β-*n*-octyl bromide has been shown[1] to lead to optically active β-nitro-*n*-octane and β-*n*-octyl nitrite. In view of the heterogeneous nature of this reaction it occurred to us that reaction complexes of the type I and II with the indicated electronic shifts would account for the retention of optical activity in the products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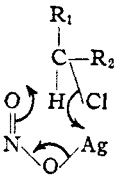
II

equally as does the assumption of a simple displacement of chloride ion by nitrite ion, the sense of the attack of the latter determining whether nitro compound or nitrite is the product. As a test of our hypothesis we have carried out the reaction of silver nitrite with *d*-α-phenethyl chloride in benzene, in which case a retention of optical activity would be expected if cyclic complexes of the type shown were intermediates. Our choice of the optically active halide was dictated by the observation that if activity were retained in this case, the experiment would constitute good evidence for the hypothetical mechanism, since it has been shown[2] that in the reaction of benzyl chloride with mercuric salts, the mercuric ion simply removes the halogen leaving the alkyl residue as a carbonium ion or its equivalent. If the silver ion of the silver nitrite operates in this latter sense rather than in the former in the case of *d*-α-phenethyl chloride, the formation of α-phenethyl nitrite and α-nitroethylbenzene should be attended with racemization.

Our experiments show that racemization is the predominant course of the reaction in question.

Experimental

***d*-α-Phenethyl Chloride.**—This material was obtained from *d*-α-phenethyl alcohol[3] ($[\alpha]^{32}D$ +29.8°) by the method of McKenzie and Clough.[4] Our material had b. p. 85–86° at 29 mm., $n^{25}D$ 1.5250 and $[\alpha]^{32}D$ + 37.0°.

***d*-α-Phenethyl Nitrite.**—A mixture of 3.5 g. of sodium nitrite, 10 cc. of water and 6.1 g. *d*-α-phenethyl alcohol ($[\alpha]^{32}D$ +29.8°) was cooled in an ice-bath and treated with 8.5 cc. of 6 *N* hydrochloric acid in portions during fifteen minutes with swirling. The layers were then separated, the product was diluted with ether, dried over sodium sulfate, freed from solvent and distilled through a two-foot Podbielniak column to yield 4.5 g. of *d*-α-phenethyl nitrite, a yellow oil of turpentine odor, of b. p. 70–71° at 16 mm.,[5] of $n^{25}D$ 1.4912, and of $[\alpha]^{31}D$ +39.9°.

Reaction of *d*-α-Phenethyl Chloride with Silver Nitrite.—Eight and one-half grams of *d*-α-phenethyl chloride ($[\alpha]^{32}D$ +37.0°) and 12.2 g. of silver nitrite (dried *in vacuo* over phosphorus pentoxide) were shaken together in 100 cc. of dry benzene for twelve hours. The silver halide was filtered off, the benzene was removed *in vacuo*, and the product was distilled through a two-foot Podbielniak column. The following fractions were obtained:

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[1] Shriner and Young, THIS JOURNAL, **52**, 3332 (1930).

[2] Roberts and Hammett, *ibid.*, **59**, 1063 (1937).

[3] We wish to express our appreciation to George DeLaMater of Harvard University for providing us with the active phenethyl alcohols.

[4] McKenzie and Clough, *J. Chem. Soc.*, **103**, 687 (1913).

[5] *d*-α-Phenethyl nitrite has been previously reported as a yellow oil of b. p. 72.5–73° at 19 mm. [Holmberg, *Ber.*, **45**, 999 (1912)].

Fraction	B. p. °C.	Mm.	Grams	n^{25}D	$[\alpha]^{25}$D
1	45–46.5	4	1.3	1.4909	+5.1
2	46.5–80	4	2.9	1.4932	+5.1
3	80–89	4.5	0.7	1.5110	...
4	89–95	5	1.9	1.5095	+2.4

Fraction 1 was concluded to be essentially pure α-phenethyl nitrite. In order to establish the nature of fraction 4, 50 g. of *dl*-α-phenethyl chloride was treated with silver nitrite under the conditions described above, and from the crude reaction product there was obtained by repeated fractionation, in addition to 11.5 g. of α-phenethyl nitrite of b. p. 34–36° at 2 mm. and of n^{25}D 1.4938, 2.5 g. of colorless oil of b. p. 90–95° at 3 mm. and of n^{25}D 1.5210. The latter material,.which corresponded roughly to fraction 4 above, was shown to contain largely α-nitroethylbenzene by conversion to the aci-form according to the method of Bamberger and Seligman.[6] The intermediate fractions gave precipitates of silver chloride when warmed with alcoholic silver nitrate solution and were concluded to contain, in addition to the other two components, unreacted α-phenethyl chloride.

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[6] Bamberger and Seligman, *Ber.*, **36**, 707 (1903).

CONVERSE MEMORIAL LABORATORY
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RECEIVED JULY 19, 1946

Catalytic Decomposition of DDT

BY A. L. FLENNER

From work conducted on the stability of DDT to heating at 115°, Fleck and Haller[1] concluded that impurities present in technical DDT inhibit the action of catalytic substances in eliminating hydrogen chloride, and that removal of these impurities without simultaneous removal of catalytic substances produces an apparent instability of DDT. In the course of work on the manufacture and formulation of DDT, this Laboratory made a study of the stability of samples varying in degrees of purity.

It was found that Technical DDT, having a set point of 88°, and highly purified material, with a melting point of 108.5°, evolved no hydrogen chloride when heated for twenty-four hours at 115°, whereas material which had been once recrystallized from ethanol, and having a melting point of 105–107°, did evolve hydrogen chloride when heated under the same conditions. The material melting at 105 to 107° had not been filtered from a small amount of insoluble impurities during the recrystallization and it was thought that these impurities might be acting as catalytic decomposing substances. A portion of the partially purified material was therefore dissolved in ethanol, filtered, and then the solution evaporated to dryness to recover the DDT. When this filtered DDT, after drying, was subjected to heating at 115° for twenty-four hours, it was found to be stable since no hydrogen chloride was evolved, which indicates that the insoluble impurities acted as catalytic decomposition agents and their removal rendered the DDT stable under the test conditions. To obtain additional evidence, both technical DDT and purified DDT of m. p. 108.5° were heated in the presence of iron oxide at 115°. Hydrogen chloride was evolved almost immediately from different samples of the purified material, while from four to six hours were required to evolve hydrogen chloride from samples of technical DDT.

These results therefore verify those of Fleck and Haller[1] and it is concluded that there is some substance or substances present in technical DDT which act as an inhibitor to the catalytic elimination of HCl. Removal of these inhibiting substances will render the DDT susceptible to catalytic decomposition. It, therefore, seems quite possible that under conditions of use technical DDT may be more stable than purified or partially purified material since catalytic substances present in diluents and natural dusts may act to liberate hydrogen chloride slowly from spray deposits of the purified DDT. Although purified DDT is not being used extensively at the present time any future use under field conditions may require the addition of an inhibitor to protect it from catalytic decomposition.

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[1] Fleck and Haller, THIS JOURNAL, **68**, 142 (1946).

PEST CONTROL RESEARCH LABORATORY
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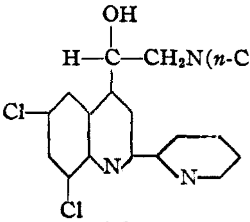
WILMINGTON, DELAWARE
RECEIVED AUGUST 5, 1946

6,8-Dichloro-2-(2'-pyridyl)-α-di-*n*-butylaminomethyl-4-quinolinemethanol[1a]

BY HENRY GILMAN, LEO TOLMAN AND SAMUEL P. MASSIE, JR.

In connection with studies on experimental avian malaria it was desirable to determine the activity of a 6,8-dichloro-4-quinolinemethanol having a nitrogen heterocycle in the 2-position. The compound selected was 6,8-dichloro-2-(2'-pyridyl) - α - di - *n* - butylaminomethyl-4-quinolinemethanol.[1b] This compound [I] was prepared *via* the Pfitzinger reaction by condensation of 5,7-dichloroisatin with methyl α-pyridyl ketone.[2] Ethyl 6,8-dichloro-2-(2'-pyridyl)-cinchoninate was prepared incidental to an examination of its condensation with ethyl acetate to give the corresponding ketoester. The plan was to brominate the keto-ester as a means of preparing the 4-bromoacetyl compound. However, some orienting experiments showed that the condensation of the ethyl ester with ethyl acetate by means of sodium ethoxide was not so satisfactory as the reaction of diazomethane with the acid chloride.



[I]

Experimental

6,8-Dichloro-2-(2'-pyridyl)-cinchonic Acid.—A mixture of 77 g. (0.36 mole) of 5,7-dichloroisatin,[3] 60 g. (1.08

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[1] (a) The work described in this paper was done under a contract recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Iowa State College; (b) the Survey Number assigned to this drug by The Survey of Antimalarial Drugs is SN-14,143-4. The activities of these compounds will be tabulated in a forthcoming monograph.

[2] See Winstein, Jacobs, *et al.*, THIS JOURNAL, **68**, 1831 (1946). Also, Lindwall, Bandes, and Weinberg *ibid.*, **53**, 317 (1931).

[3] Prepared in accordance with directions kindly provided by Drs. H. Sargent and T. C. Myers of the California Institute of Technology.