chloride and the precipitate was washed with five portions of fresh solvent and dried on the vacuum line to give 95% of the nitrilium salt as a pale yellow powder, m.p. 230–233° to a scarlet melt (reported[3,2] 231–234°, 236–237°).

Reaction of N-phenylbenzonitrilium hexachloroantimonate with aniline. A solution of 0.58 g. (0.0062 mole) of aniline in 25 ml. of dry benzene was treated with 2.93 g. (0.0057 mole of II and the mixture was worked up as described for the reaction of I, giving 1.53 g. of yellow solid. Chromatography of a 0.63 g. aliquot on 13 g. of Merck alumina gave 0.38 g. of *N,N'*-diphenylbenzamidine, m.p. 145.7–147° (reported[14] 146.5–147°), eluted by 320 ml. of methylene chloride-hexane, 1:1. The yield is thus 59%. The analytical sample was crystallized three times from isopropanol (recovery, 89%) and sublimed at one micron and 135°.

Anal. Calcd. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.77; H, 5.95; N, 10.41.

The *picrate* was prepared in benzene, m.p. 218–219° (reported[14] 221°).

Reaction of N-phenylbenzonitrilium hexachloroantimonate with phenol. A mixture of 4.36 g. (0.00847 mole) of the nitrilium salt and 1.0 g. (0.0106 mole) of phenol in 25 ml. of dry benzene was kept overnight at room temperature, refluxed for 15 min. and finally treated with cold, aqueous alkali to *p*H 10. Working up as in the preceding section provided 2.18 g. of yellow solid. A 0.60-g. aliquot chromatographed on 18 g. of Merck alumina gave 0.325 g. of phenyl *N*-phenylbenzimidoate, m.p. 104–105°, eluted by 50 ml. of benzene-hexane, 3:1, yield, 51%. The analytical sample was crystallized twice from hexane and sublimed at one micron and 92°, m.p. 104.5–106° (reported[14] 104.5–105°).

Anal. Calcd. for $C_{19}H_{15}NO$: N, 5.13. Found: N, 5.14.

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Nitrosation of Acylated 1,2-Diaminoethenes[1]

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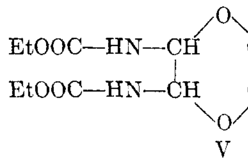
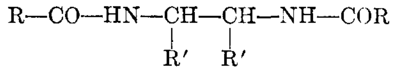
Acylated 1,2-diaminoethanes have been reported in the literature to react normally with nitrous acid to the expected bis-*N*-nitroso derivatives.[2] As reported in this paper the reaction of acylated 1,2-diaminoethenes takes an entirely different course.

Starting materials for this investigation were 1,2-di(benzoylamino)ethene[3] (I) and 1,2-di(carbethoxyamino)ethene (II). The latter compound could not be obtained *via* the Curtius degradation of fumaric acid as reported in the literature.[4] An isomer, probably the *cis*-II, however, was easily obtained by the Bamberger cleavage of imidazole with ethyl chloroformate and alkali. The identity of the *cis*-II was confirmed by catalytic hydrogenation to the known 1,2-di(carbethoxyamino)ethane. Both I and II reacted in alcoholic solution with ethyl or isoamyl nitrite in the presence of hydrochloric acid with immediate development of an intense blue-green color which soon disappeared whereupon colorless crystals deposited. These crystals turned out to be the corresponding 1,2-diethoxy-1,2-di(carbethoxyamino)ethanes (IIIa, resp. IIIb). Replacement of ethanol by isopropylalcohol in this reaction led from II to the corresponding isopropoxy compound IV while ethylene glycol yielded the dioxane derivative V. In an aqueous system the glycol VI was obtained from I with sodium nitrite and hydrochloric acid. Compounds IIIa and VI have previously been obtained from I *via* the dibromide VII.[3] In the case of IIIa we obtained apparently a stereoisomer, m.p. 240–241°, whereas Ruggli reports two isomers, m.p. 190–191°, and m.p. 219° *via* his route. The glycol VI was obtained as a mixture of two stereoisomers, m.p. 162–164°, and m.p. 180–182°, while Ruggli isolated in this case only the lower melting isomer. It is obvious the glycol and its ethers can occur both as meso- and racemic forms. When the nitrosation of II with isoamyl nitrite and alcoholic hydrogen chloride was carried out for a prolonged period, the originally formed crystals of IIIb went again into solution. A new compound could then be isolated which derived from IIIb by the loss of one molecule of alcohol. Presumably, ring closure to 1-carbethoxy-4,5-diethoxyimidazolidinone-2 (VIII) occurred.

R—CO—HN—CH=CH—NH—CO—R
I. R = C_6H_5, II. R = OEt

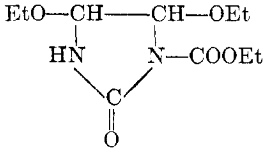


V



$$R{-}CO{-}HN{-}\underset{R'}{\underset{|}{CH}}{-}\underset{R'}{\underset{|}{CH}}{-}NH{-}COR$$

IIIa. R = C_6H_5 IIIb. R = OEt
R' = OEt R' = OEt
VI. R = C_6H_5 IV. R = OEt
R' = OH R' = $OCH(CH_3)_2$
VII. R = C_6H_5
R' = Br



VIII

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(1) This article is based on work performed under Project 116 B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corp., New York, N. Y.

(2) H. Holter and H. Bretschneider, *Monatsh.*, **53/54**, 963 (1929); C. M. Samour and J. P. Mason, *J. Am. Chem. Soc.*, **76**, 441 (1954); T. Lieser and G. Beck, *Chem. Ber.*, **84**, 137 (1950); H. Lettre and U. Brose, *Naturwissenschaften*, **36**, 57 (1949).

(3) P. Ruggli, R. Ratti, and E. Henzi, *Helv. Chim. Acta*, **12**, 332 (1929).

(4) R. Radenhausen, *J. prakt. Chem.*, [2] **52**, 453 (1895).

The observed abnormal course of the nitrosation of acylated 1,2-diaminoethenes with formation of highly reactive addition products to the double bond which on subsequent alcoholysis or hydrolysis yield the corresponding alkoxy derivatives or glycols is apparently caused by the two electron-releasing groups symmetrically positioned to the thereby activated double bond. Similar reactions have already been observed by Ruggli *et al.* in the case of I[3] and with 3,4-diphenylimidazolinone-2.[5] The well-known oxidation of uric acid to uric acid glycol may also belong to this kind of reaction.[6]

EXPERIMENTAL[7]

Starting materials. The *1,2-di(benzoylamino)ethene* (I) was obtained according to Ruggli[3] in a 77% yield, m.p. 212–213°, while *1,2-di(carbethoxyamino)ethene* (II) was prepared similarly from imidazole (5 g.) and ethyl chloroformate (50 g.) at 0°. The crude product of 14.4 g. (96.5%) was recrystallized from ligroin or aqueous alcohol to yield colorless crystals, m.p. 139–141°.

Anal. Calcd. for $C_8H_{14}N_2O_4$: C, 47.51; H, 6.97; N, 13.85. Found: C, 47.48; H, 6.90; N, 13.89.

II is soluble in concd. hydrochloric acid but after several minutes at room temperature the color of the solution changes to a greenish black due to decomposition.

To 2 g. of II in 60 ml. of absolute alcohol 20 mg. of $PdCl_2$ was added and the mixture hydrogenated at room temperature. The calculated amount of hydrogen was consumed in 44 min. The Pd was filtered off and after evaporation of the alcohol *in vacuo* 1.7 g. (85%) of 1,2-di(carbethoxyamino) ethane, m.p. 114°, was obtained. The mixed melting point with an authentic sample prepared from ethylenediamine and ethyl chloroformate[8] showed no depression.

1,2-Diethoxy-1,2-di(benzoylamino)ethane (IIIa). To a suspension of I (2 g.) in 50 ml. of absolute alcohol isoamyl nitrite (1.8 g.) was added and dry hydrogen chloride bubbled through the reaction mixture at 0°. A blue green coloration developed immediately and within 2 hr. all material went into solution. Water was added to the now colorless, ice-cooled reaction mixture whereupon 1.3 g. (49%) of crude IIIa, m.p. 169–173°, separated. After one recrystallization from ethanol the melting point rose to 240–242°.

Anal. Calcd. for $C_{20}H_{24}N_2O_4$: C, 67.39; H, 6.78; N, 7.85. Found: C, 67.27; H, 6.78; N, 7.89.

1,2-Diethoxy-1,2-di(carbethoxyamino)ethane (IIIb) was obtained analogously from II (3 g.) and isoamyl nitrite (3.5 g.). Also in this case an immediate deep blue coloration was observed which changed soon to dark green, whereupon crystallization of IIIb started. After 20 min. 1.6 g. (37%) of colorless needles, m.p. 148°, were obtained. After one recrystallization from water IIIb melted at 151–152°.

Anal. Calcd. for $C_{12}H_{24}N_2O_6$: C, 49.30; H, 8.27; N, 9.58. Found: C, 49.18; H, 8.29; N, 9.69.

With an excess of ethyl nitrite instead of isoamyl nitrite the reaction yielded IIIb in a 69% yield. With isopropyl alcohol and isoamyl nitrite II yielded 57% of *1,2-diisopropoxy-1,2-di(carbethoxyamino)ethane* (IV), colorless needles from aqueous isopropyl alcohol, m.p. 159–161°.

Anal. Calcd. for $C_{14}H_{28}N_2O_6$: C, 52.48; H, 8.81; N, 8.74. Found: C, 52.81; H, 8.49; N, 8.74.

The reaction of II (1 g.) with isoamyl nitrite (1 g.) and hydrogen chloride in ethylene glycol (30 ml.) yielded analogously *2,3-di(carbethoxyamino)-1,4-dioxane* (V) (1.1 g., 85%), colorless needles after recrystallization from ethanol, m.p. 190–191°.

Anal. Calcd. for $C_{10}H_{18}N_2O_6$: C, 45.79; H, 6.91; N, 10.67. Found: C, 45.80; H, 6.75; N, 10.76.

1,2-dihydroxy-1,2-di(benzoylamino)ethane (VI). A solution (1.1 g.) of sodium nitrite in 10 ml. of water was added dropwise at 0° to a suspension of I (2 g.) in 100 ml. of concd. HCl. Each drop caused immediately a blue coloration which faded quickly to yellow. After stirring for 1 hr., 1 g. of unchanged starting material was filtered off. Addition of water to the filtrate yielded a crystalline precipitation of VI (0.8 g., 70%), m.p. 168–177°. Repeated recrystallization from alcohol separated this material into approximately equal amounts of a more soluble fraction, m.p. 162–164° and into a soluble fraction, m.p. 180–182°. The lower melting product was identical with the product obtained by Ruggli.[3] The higher melting isomer gave the following analytical data:

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.98; H, 5.37; N, 9.33. Found: C, 63.55; H, 4.98; N, 9.53.

When the higher melting isomer was sublimed in a vacuum benzamide, m.p. 132–133°, was obtained besides polyglyoxal. An attempted hydrolysis of VI with 40% aqueous KOH yielded benzoic acid as the only isolable product.

1-Carbethoxy-4,5-diethoxyimidazolidinone-2 (VIII). When the reaction of II (3 g.) and isoamyl nitrite (3.5 g.) in absolute ethanol with hydrogen chloride was carried on for 2 hr., the originally formed crystals went again into solution. To remove the excess of hydrochloric acid, potassium carbonate was added and then the solvent removed *in vacuo*. The residue was extracted with boiling ethanol from which 1.1 g. (30%) of VIII crystallized on cooling. M.p. 200–202°.

Anal. Calcd. for $C_{10}H_{18}N_2O_5$: C, 48.78; H, 7.36; N, 11.37. Found: C, 49.02. H, 7.43; N, 11.03.

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(5) H. Biltz, Ann., **368**, 156, 262 (1909).

(6) H. Biltz and H. Schauder, *J. prakt. Chem.* [2], **106**, 169 (1923).

(7) Melting points are uncorrected (Fisher-Johns); analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(8) E. Fischer and H. Koch, *Ann.*, **232**, 228 (1885).

Benzo-1,2,3-triazines

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Recent work has demonstrated that aminochlorobenzo-1,2,4-triazines possess remarkable pharmacological properties.[2] It seemed, therefore, of interest to investigate some representatives of the benzo-1,2,3-triazine series.

Benzo-1,2,3-triazines substituted in the 4-position are generally obtained by the diazotization of *o*-aminobenzoic acid derivatives. The desired 4-aminobenzo-1,2,3-triazine (I) and 4-hydrazinobenzo-1,2,3-triazine (II), however, were not accessible by this route, since *o*-aminobenzamidine and *o*-aminobenzamidrazone could not be prepared from *o*-aminobenzonitrile. The reluctance of *o*-

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(1) This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, New York, N. Y.

(2) F. J. Wolf, K. Pfister, R. M. Wilson, Jr., and C. A. Robinson, *J. Am. Chem. Soc.*, **76**, 3551 (1954); F. J. Wolf, R. M. Wilson, Jr., K. Pfister, and M. Tishler, *J. Am. Chem. Soc.*, **76**, 4611 (1954).