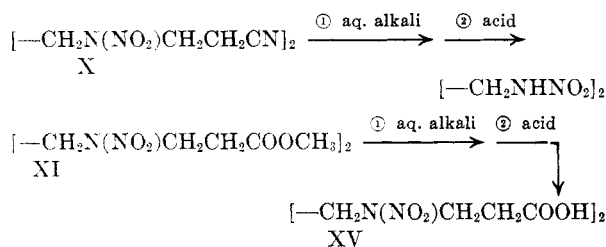


mine and decomposition products of acrylonitrile while dimethyl 4,7-dinitro-4,7-diazadecanedioate (XI) under the same conditions is converted to the anion of 4,7-dinitro-4,7-diazadecanedioic acid (XV) which is stable in excess alkali.



EXPERIMENTAL

Methyl- and ethylnitramine, ethylenedinitramine, and *N*-methylethylenedinitramine were prepared as described by Franchimont and Klobbie;⁷ *n*-butylnitramine was obtained by the method of van Erp.⁸

Michael additions: Method A. A mixture of the nitramine, 1.3–2.0 equivalents of the conjugated unsaturated compound, and a few drops of Triton B (commercial trimethylbenzyl ammonium hydroxide solution) was heated with stirring as specified in Table I. The progress of the reaction was followed by observing the relative intensities of the primary and secondary nitramine bands in the infrared. At the end of the reaction period the mixtures, except where noted, were poured into water and ether extracted. After decolorizing with charcoal and drying, solvent was removed

(7) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 343, 347, 354, and 356 (1888).

(8) M. H. van Erp, *Rec. trav. chim.*, **14**, 26 (1895).

from the ether extracts and liquid mixtures were separated by distillation through a small Vigreux column; solid residues were purified by recrystallization from aqueous ethanol or methanol.

Method B. A solution of the sodium or potassium salt of the nitramine in 50% aqueous methanol was stirred while an equivalent weight of the conjugated unsaturated compound was added. After treating the mixture as specified in Table I, the product was isolated by diluting with an equal volume of cold water and extracting with ether. The dried ether extracts were then treated as described under Method A.

Action of alkali on 4,7-dinitro-4,7-diazadecanedinitrile (X). A suspension of 1 g. of 4,7-dinitro-4,7-diazadecanedinitrile (0.004 mole) in 6 ml. of water containing 1.3 g. (0.02 mole) of 85% potassium hydroxide was warmed on a steam bath for 1 hr. during which the suspension slowly cleared and ammonia was evolved. After chilling and acidification with 25% sulfuric acid, 0.49 g. (82%) of ethylenedinitramine, m.p. 174–178°, was obtained. The infrared spectrum of this sample in acetonitrile was indistinguishable from that of authentic ethylenedinitramine.

Action of alkali on dimethyl 4,7-dinitro-4,7-diazadecanedioate (XI); preparation of 4,7-dinitro-4,7-diazadecanedioic acid (XV). A suspension of 1 g. of dimethyl 4,7-dinitro-4,7-diazadecanedioate (0.003 mole) in 10 ml. of water containing 1.0 g. (0.018 mole) of 85% potassium hydroxide was warmed on a steam bath for 1 hr., cooled to room temperature, and acidified with concentrated hydrochloric acid. After chilling the mixture, 0.67 g. (76%) of 4,7-dinitro-4,7-diazadecanedioic acid (XV), m.p. 134.5–136.5°, was collected by filtration. Recrystallization from water gave plates melting at 142–143°, (Gold⁴ gave the melting point of this compound as 141.5–142.5°.)

Anal. Calcd. for C₈H₁₄N₄O₈: C, 32.66; H, 4.80; N, 19.04; *neut. equiv.* 147. Found: C, 32.24; H, 4.58; N, 18.68; *neut. equiv.* 147.

LOS ALAMOS, N. M.

[CONTRIBUTION No. 830 FROM THE CHEMISTRY LABORATORIES OF INDIANA UNIVERSITY]

Reaction of Diethyl Oxalate with Some *ortho*-Substituted Anilines¹

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Ethyl 2-benzothiazolecarboxylate (I) may be obtained in excellent yield by refluxing *o*-aminobenzenethiol with excess diethyl oxalate. However, *o*-aminophenol condenses with diethyl oxalate to yield a different type of product, the oxanilide III, while *o*-phenylenediamine formed still a third type of condensation product, the quinoxaline IV. The nature of the condensation products in these reactions was not altered by varying the conditions.

In connection with another problem, it was desirable to obtain large samples of esters of heterocyclic carboxylic acids, such as 2-benzothiazolecarboxylic acid. Ethyl 2-benzothiazolecarboxylate (I) has been previously prepared from the acid,³ which, in turn, was prepared in several steps from

(1) This work was supported by a contract between the Office of Naval Research, Department of the Navy, and Indiana University.

(2) Taken in part from the thesis of J. E. Van Verth, presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University, 1957.

(3) (a) S. G. Fridman, *Zhur. Obshchei Khim.*, **20**, 1191 (1950); *Chem. Abstr.*, **45**, 1579 (1951); (b) A. Reissert, *Ber.*, **37**, 3708 (1904).

other 2-substituted benzothiazoles.⁴ A direct and more convenient method for preparing this ester from commercially available materials has now been found, which involves the condensation of 2-aminobenzenethiol with diethyl oxalate.

Hofmann,⁵ in 1880, isolated 2,2'-bibenzothiazolyl (II) when these reactants were heated for "a long time and at a high temperature." It seemed reasonable that the reaction proceeded through the

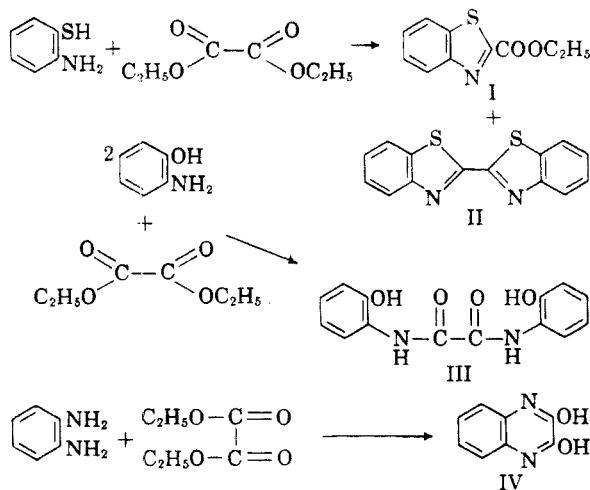
(4) (a) H. Gilman and J. A. Beel, *J. Am. Chem. Soc.*, **71**, 2328 (1949); (b) Y. Mizuno, *J. Pharm. Soc. Japan*, **72**, 1263 (1952); (c) H. Salkowski and W. Kunze, German Patent 613,067, May 11, 1935; *Chem. Abstr.*, **29**, 5461 (1935).

(5) A. W. Hofmann, *Ber.*, **13**, 1223 (1880).

intermediate I, which presumably would react slowly enough to be isolated. It was found that I could be obtained by refluxing the reactants in a molar excess of diethyl oxalate for four hours. The ester was isolated by pouring the resulting solution into a mixture of dilute hydrochloric acid and ethanol which dissolved the excess ethyl oxalate and unreacted aminothiol, so that I could solidify and be removed by filtration. The crude ester, obtained in 80% yield, was contaminated with about 6% by weight of crude II, which was removed by virtue of the latter's insolubility in hot petroleum ether, from which I readily crystallized. Although quite insoluble in most solvents, II was easily crystallized from dioxane.

This synthesis of ethyl 2-benzothiazolecarboxylate achieves in one step what previously required four to six steps, by way of the acid. Indeed, the hydrolysis of the ester prepared in this way may provide the most convenient route to the acid itself, and no doubt *benz*-substituted analogs could be prepared similarly, contingent on the availability of the necessary *o*-aminothiols.

In view of this result, we decided to reinvestigate the reactions of diethyl oxalate with *o*-phenylenediamine and *o*-aminophenol, in the hope of obtaining esters of 2-benzimidazolecarboxylic acid and 2-benzoxazolecarboxylic acid. A one- or two-molar excess of oxalate ester was used as solvent; in each case only the product which had been previously reported⁶ was obtained. It is remarkable that each of the three *o*-substituted amines gave a different type of product.



Although Reissert and Goll⁷ had reported that the reaction of 4-nitro-2-aminodiphenylamine with diethyl oxalate produced some benzimidazole ester in addition to the quinoxaline, all efforts to isolate ethyl 2-benzimidazolecarboxylate from the reaction mixture of *o*-phenylenediamine with diethyl oxalate were unavailing; only 2,3-quinoxalinediol

(IV) was obtained. Since acid catalysts might promote the ring closure, these were examined briefly. Zinc chloride increased the rate but did not change the course of the reactions of diethyl oxalate with *o*-phenylenediamine and *o*-aminophenol. Essentially the same yield (87–89%) of IV was obtained when the reactants were heated without catalyst for one hour as when they were heated at approximately the same temperature with a small amount of zinc chloride for only twenty minutes. With *o*-aminophenol, at least, the rate of reaction was apparently affected more by the temperature than by the addition of catalyst, 69% of *o,o'*-dihydroxyoxanilide (III) being obtained after one hour on the steam bath and 89% after fifteen minutes at reflux. The addition of a small amount of a solution of zinc chloride in absolute ethanol lowered the reflux temperature of the mixture to about that of a steam bath, and under these conditions 86% of III was obtained after one hour. Meyer and Seeliger⁶ had found that III was formed even when diethyl oxalate was present in large excess. In an attempt to promote the reaction of ethyl oxalate with *o*-aminophenol in a 1:1 molar ratio, one-tenth mole of the latter in pyridine was added over a period of three hours to a boiling pyridine solution of two-tenths mole of the ester, using pyridine hydrochloride as catalyst. Only III was isolated.

In the case of 2-aminobenzenethiol, the results were somewhat different. When zinc chloride in absolute ethanol was added as catalyst, the yield of I was lowered. This was undoubtedly due to the effect of the added ethanol in lowering the initial reflux temperature, which in the absence of catalyst, approached the boiling point of diethyl oxalate. In either case the temperature dropped as the reaction proceeded, because of the formation of ethanol. The catalyst apparently promoted further reaction of I with 2-aminobenzenethiol, for the amount of by-products (presumably chiefly II) formed in the presence of the catalyst was two to three times as much as without catalyst.

EXPERIMENTAL⁸

Ethyl 2-benzothiazolecarboxylate (I) from 2-aminobenzenethiol. A. Without catalyst. A mixture of 12.5 g. (0.1 mole) of 2-aminobenzenethiol and 29.2 g. (0.2 mole) of diethyl oxalate was heated at mild reflux for 4 hr., during which time the temperature decreased from 147 to 93°. After cooling, the mixture was poured into a solution consisting of 50 ml. of concentrated hydrochloric acid, 150 ml. of water, and 70 ml. of 95% ethanol. With stirring, the oil dissolved and a solid formed. The mixture was cooled in an ice bath (to 9°), the product was removed by filtration, and washed with 75 ml. of chilled aqueous ethanol (ca. 25%) in two portions, then dried overnight in a vacuum desiccator. The 16.5 g. (80%) of crude ester melted at 69–69.5° (cloudy melt). When this was recrystallized from 53 ml. of 63–99° petroleum ether, 12.5 g. of needles melting at 69.8–70.5° were obtained in two crops. The ester is reported^{3a,b} to melt at 70–71°.

(6) R. Meyer and A. Seeliger, *Ber.*, **29**, 2640 (1896).

(7) A. Reissert and G. Goll, *Ber.*, **38**, 90 (1905).

(8) Melting points are uncorrected. The authors are indebted to Miss Joanna Dickey for microanalyses.

Anal. Calcd. for $C_{10}H_9O_2NS$: N, 6.76. Found: N, 6.77.

A small amount (1.0 g.) of solid melting about 175–250° was insoluble in the hot petroleum ether. This was boiled with about 100 ml. of toluene; the hot mixture was filtered, and the filtrate was cooled in the refrigerator to produce 0.09 g. of crystals of 2,2'-bibenzothiazolyl (II), which were removed and washed with toluene and benzene. The tan platelets melted at about 310°. A melting point of "about 300°" was reported by Hofmann.⁵ The analytical sample, white platelets, was obtained by recrystallizing from dioxane and washing with ether.

Anal. Calcd. for $C_{14}H_9N_2S_2$: N, 10.44. Found: N, 10.37.

B. With zinc chloride catalyst. A mixture of 12.5 g. (0.1 mole) of 2-aminobenzenethiol, 29.8 g. (0.2 mole) of diethyl oxalate, and 5 ml. of a 2*M* solution of fused zinc chloride in absolute ethanol was boiled under reflux for 4 hr., during which time the temperature decreased from 108 to 92°. After cooling, the solution was filtered to remove a small amount of inorganic solid, then worked up as in part A. The 14.4 g. (70%) of crude product, m.p. 69–69.5° (very cloudy melt), on recrystallization from 47 ml. of 63–99° petroleum ether, produced 7.1 g. of crystals melting at 69.8–70.5°. An additional crop of 0.5 g. was obtained from the mother liquor. The material insoluble in the hot petroleum ether weighed 2.7 g., and melted at ca. 150–210°. Even after extraction with hot petroleum ether (63–99°), 2.0 g., melting about 160–215°, remained.

2-Benzothiazolecarboxyhydrazide. A mixture of 20.7 g. of I and 6.0 g. of hydrazine hydrate (pract.) in 30 ml. of ethanol was refluxed for 15 min., and then cooled. The light yellow crystals were collected and washed with cold ethanol. They weighed 18.5 g. (95%) and melted without further purification at 175.0–175.6°. Y. Mizuno^{4b} reported 2-benzothiazolecarboxyhydrazide to melt at 171°.

Anal. Calcd. for $C_8H_7ON_2S$: C, 49.69; H, 3.65; N, 21.73. Found: C, 49.62; H, 3.55; N, 21.83.

o,o'-Dihydroxyoxanilide (III) from o-aminophenol. *A. On the steam bath.* A mixture of 10.9 g. (0.1 mole) of *o*-aminophenol and 29.2 g. (0.2 mole) of diethyl oxalate was heated for 1 hr. on the steam bath. After cooling, the solid was removed and washed well with 95% ethanol. The yield was 9.4 g. (69%) of *o,o'*-dihydroxyoxanilide, melting at about 279–280° (dec.). Meyer and Seeliger⁶ reported that this compound melted at 280–282°.

B. At reflux. The reaction was carried out as in part A, except that the mixture was heated at reflux (ca. 185°) for about 15 min., instead of on the steam bath. A 12.1 g. (89%) yield, m.p. 281–282° (dec.) was obtained.

C. With zinc chloride catalyst. The reaction was carried out as in part A, except that 5 ml. of a 2*M* solution of fused zinc chloride in absolute ethanol was added and the mixture heated under reflux for 1 hr. (The temperature fell from 109 to 91°), and worked up as before. The granular solid weighed 11.7 g. (86%) and melted at 283.5–284° (dec.).

When the reactants were heated under reflux in 55 ml. of 95% ethanol containing 0.5 g. of fused zinc chloride, only 3.9 g. (29%) of product was obtained on cooling.

D. With pyridine hydrochloride catalyst in pyridine. A stream of dry hydrogen chloride was passed into 500 ml. of dry pyridine to produce a weight increase of about 6 g. (0.16 mole). After the addition of 30.3 g. (0.207 mole) of diethyl oxalate, the solution was boiled under reflux while a solution of 10.9 g. (0.1 mole) of *o*-aminophenol in 200 ml. of pyridine was added dropwise, with stirring, over a period of 3 hr. After being heated for an additional 15 min., the solution was allowed to cool and divided into 2 equal parts. One part was poured slowly, with stirring, into 2 l. of water. The pink precipitate was removed and washed with water. A 4.4 g. (65%) yield of III was obtained. About 300 ml. of pyridine was distilled from the second half of the solution, which was then treated with 200 ml. of water, to yield 6.6 g. (97%) of III.

2,3-Quinoxalinediol (IV) from o-phenylenediamine. *A. Without catalyst.* A mixture of 10.8 g. (0.1 mole) of *o*-phenylenediamine (Eastman Kodak) and 43.9 g. (0.3 mole) of diethyl oxalate was heated for 1 hr. on the steam bath. After cooling, the solid was removed and washed with 95% ethanol. The yield was 14.4 g. (89%) of a gray-green solid, not melting below 300°, as reported by Meyer and Seeliger.⁶ After recrystallization from methanol by Soxhlet extraction, the pure material decomposed at 372–373° (Fieser block).

Anal. Calcd. for $C_8H_6O_2N_2$: C, 59.25; H, 3.73. Found: C, 59.41; H, 3.67.

B. With zinc chloride catalyst. A mixture of 10.8 g. (0.1 mole) of *o*-phenylenediamine and 29.2 g. (0.2 mole) of diethyl oxalate was treated with 5 ml. of 2*M* solution of fused zinc chloride in absolute ethanol, and heated to boiling. Solid formed in the mixture very rapidly. After the mixture had refluxed for about 20 min., the temperature decreasing from about 100° to 83°, it was allowed to cool, filtered, and the solid washed with 95% ethanol. After combining with a small amount that separated from the filtrate, a yield of 14.1 g. (87%) of IV was obtained.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

A Study of the Alkylation of 2-Phenylbutanenitrile with Butyl Chlorides¹

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2-Phenylbutanenitrile has been alkylated with the butyl chlorides, using both sodamide and sodium hydride as condensing agents. With sodium hydride, the yields of products were found to be from 3 to 15% less than with sodamide. As predicted on the basis of Newman's *six-member* concept, the highly hindered nitriles thus produced failed to hydrolyze. The "arylation" and alkylation of propionitrile has also been investigated briefly.

Previous papers from this laboratory have reported the alkylation of hydratroponitrile Ia with

butyl² and amyl halides³ (see equation page 1347).

In a continuation of these studies 2-phenylbu-

(1) Based in part on the M.S. thesis of Andrew A. Holzschuh, Michigan State University, June 1955. Presented at the 130th meeting of the American Chemical Society, Atlantic City, N. J., September 16–21, 1956.

(2) G. L. Goerner and W. R. Workman, *J. Org. Chem.*, **19**, 37 (1954).

(3) R. L. Jacobs and G. L. Goerner, *J. Org. Chem.*, **21**, 837 (1956).