[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Synthesis of Imidazoles and Oxazoles from α-Diketone Monoximes[1]

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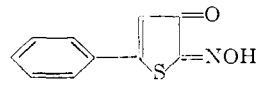
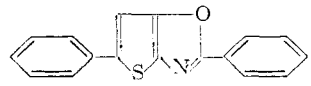
RECEIVED APRIL 13, 1955

5-Phenyl-2,3-thiophenequinone-2-oxime reacts with aromatic aldehydes to yield substituted thieno[2,3-*d*]oxazoles; other α-diketone monoximes yield the corresponding imidazoles. A possible explanation of this behavior is discussed.

During an attempt to convert 5-phenyl-2,3-thiophenequinone-2-oxime (I) to the quinone, a solution of I in excess benzaldehyde was refluxed for 24 hours, leading to the isolation of a colorless, neutral compound II which responded negatively to tests for functional groups,[3] did not form a molecular complex with 2,4,7-trinitrofluorenone,[4] and exhibited a purple-blue fluorescence under ultraviolet light. The elemental analysis corresponded to the formula $C_{17}H_{11}ONS$, the ultraviolet absorption spectrum had a maximum at 338 mμ, log ε 4.53, and the infrared spectrum indicated the presence of a monosubstituted phenyl group[5,6] and, possibly, a C=N group in a conjugated ring (6.76 μ)[7] and an ether linkage (8.38 μ).[5] A plausible structure consistent with these data appeared to be 2,5-diphenylthieno[2,3-*d*]oxazole. Yields of II as high as 48% were obtained when an 18-hour reaction time was employed and the temperature was kept at 180° (refluxing benzaldehyde). When I was refluxed at a lower temperature in a 33% solution of benzaldehyde in *m*-xylene the yield of II was 37%, and from a 10% solution of benzaldehyde in benzene most of



I



II

the oxime was recovered unchanged which was also the case when solutions in ethanol and diisopropyl ether were employed. Anisaldehyde, cumaldehyde and *p*-tolualdehyde were converted into the corresponding substituted diphenylthienoöxazoles; cinnamaldehyde yielded traces of an unidentified fluorescent material, and from the reaction with *n*-hexaldehyde, the one aliphatic aldehyde investigated, no crystalline product could be obtained.

The structure assigned to II is supported by the reports of somewhat analogous oxazole syntheses in the literature. Diels and Riley[8] and Dilthey and Friedrichsen[9] isolated oxazole N-oxides from the reaction of α-diketone monoximes and benzaldehyde in the presence of hydrogen chloride or hydrochloric acid. Reduction with zinc then converted the oxide to the oxazole. Japp and Wilcock[10] showed that *o*-quinones are transformed into oxazoles when heated with aromatic aldehydes in the presence of ammonia or an ammonia precursor, a reaction which has been studied by a number of investigators.[11]

Although we were able to convert benzil monoxime, biacetyl monoxime and 1,2,3-cyclohexanetrione-1,3-dioxime to the corresponding oxazole N-oxides by treating them with benzaldehyde and hydrogen chloride in acetic acid,[8,9] I was largely unchanged under both the same and modified experimental conditions. Utilizing the reaction conditions under which I was transformed into II, biacetyl monoxime gave a mixture of intractable tar and recovered oxime; 1,2,3-cyclohexanetrione-1,3-dioxime decomposed completely when refluxed for 18 hours, and was largely recovered unchanged when the reaction was carried out at room temperature for three days; 9,10-phenanthrenequinone monoxime yielded phenanthra[9,10-*d*]imidazole; and benzil monoxime gave lophine (III), 2,3,5-triphenylimidazole, in almost quantitative yield after only one hour. That benzaldehyde does not effect reduction of an oxazole N-oxide was demonstrated by refluxing triphenyloxazole N-oxide in benzaldehyde, whereupon a small amount of III, but no triphenyloxazole, could be isolated. The possibility that the oxazole was an intermediate in the formation of III is excluded by the work of Kreps and Day[11c] who found that oxazoles did not react when heated with benzaldehyde and ammonia under severe hydrolytic conditions.[12] These data would indicate that the reaction path by which I is converted into II differs signally from those by which the other isonitrosoketones react.

We attempted to determine the possible catalytic effect of various agents on the formation of II by

(1) Abstracted from a portion of the Ph.D. thesis of C. M. S., University of Cincinnati, June, 1953. (a) Ernst D. Twitchell Fellow, 1952–1953.

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(3) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

(4) M. Orchin and E. O. Woolfolk, THIS JOURNAL, **68**, 1727 (1946).

(5) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

(6) R. B. Barnes, R. C. Gore, U. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publ. Corp., New York, N. Y., 1944.

(7) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

(8) O. Diels and F. Riley, *Ber.*, **48**, 897 (1915).

(9) W. Dilthey and J. Friedrichsen, *J. prakt. Chem.*, [2] **127**, 292 (1930).

(10) F. R. Japp and E. Wilcock, *J. Chem. Soc.*, **37**, 661 (1880), and later papers.

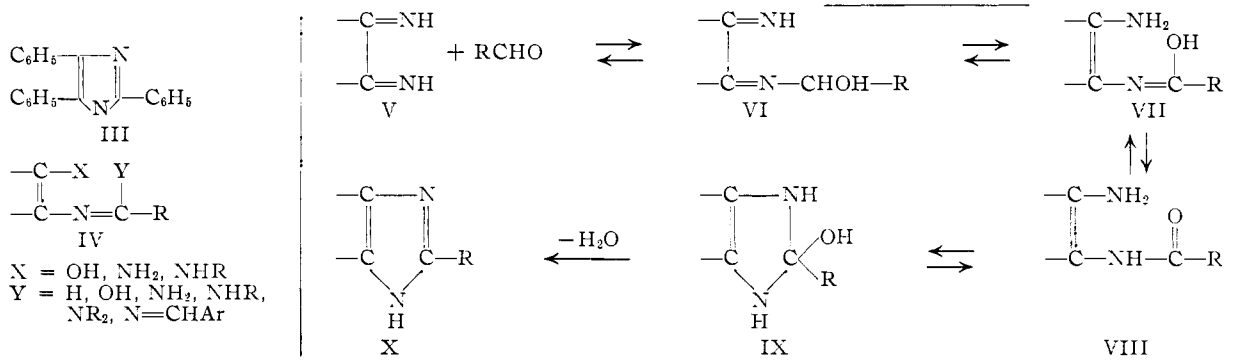
(11) *E.g.*, (a) A. C. Sircar and G. C. Sircar, *ibid.*, **123**, 1559 (1923); (b) D. Davidson, M. Weiss and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937); (c) S. I. Kreps and A. R. Day, *ibid.*, **6**, 140 (1941).

(12) H. Bredereck and G. Theilig, *Ber.*, **86**, 88 (1953), have postulated that an oxazole is the intermediate in the transformation of α,β-diketones, α-haloketones, α-aminoketones and α-isonitrosoketones (*reducing conditions only*) into imidiazoles on heating with formamide; and G. Theilig, *ibid.*, **86**, 96 (1953), has demonstrated that formamide can convert oxazoles to imidazoles under these conditions. Opening of the oxazole ring and condensation with formamide are presumably involved. We feel that this work does not invalidate our hypothesis on the course of the *benzaldehyde*-isonitrosoketone reaction since the presence of *formamide* seems to be essential for the occurrence of the transformations noted by the German workers. It is of interest to note that Theilig was unable to convert condensed ring oxazoles, *e.g.*, benzoxazole, to the analogous imidazole under his conditions, whereas 9,10-phenanthrenequinone monoxime is converted to the imidazole when heated with benzaldehyde.

stopping the reaction before completion and isolating the products. The results were too inconsistent to provide valuable information, and all that can be said is that none of the materials added had a pronounced effect on the rate of reaction. The lack of reproducibility is due to the difficulty of working up the reaction mixture.

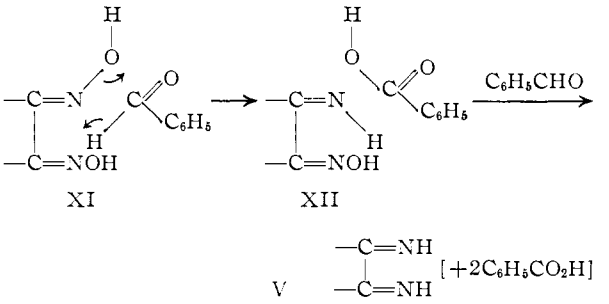
To recapitulate, we have found that certain α-diketone monoxime systems form either imidazoles or oxazoles when heated in the presence of an aromatic aldehyde. The formation of the imidazole ring must involve the transfer of a nitrogen atom from one molecule to another, the loss of oxygen, and carbon–nitrogen condensation. McCoy and Day[13] have made a comprehensive study of *ortho* condensations which lead to oxazole or imidazole formation, and concluded that most, if not all, such condensations go through a common intermediate of the type IV.

The reaction of 9,10-phenanthrenequinone diimine and aldehydes to yield phenanthrimidazoles[14] has been represented as[13,15]



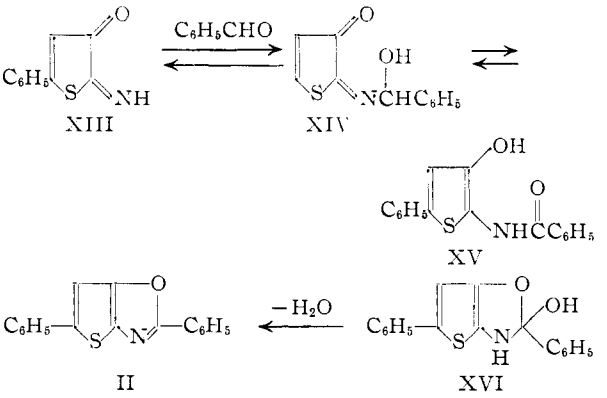
A possible explanation of the imidazole synthesis described in this paper involves a diimine intermediate.

The first step of the reaction involves a disproportionation of the diketone monoxime to the dioxime; this appears to be a reasonable assumption in the light of Lapworth's classic work on reversibility of oxime formation[16]; Ponzio's observation[17] that α-diketone monoximes in hydrochloric acid are in equilibrium with the diketones and dioximes, and that the equilibrium is well over to the right; the fact that an exchange of the oxime group occurs when a carbonyl compound is heated with an oxime; and our observation that benzil *dioxime* also forms III when heated with benzaldehyde. The second stage of the reaction, the loss of oxygen, does not go through an N-oxide stage, inasmuch as we have shown that benzaldehyde does not reduce such compounds to the parent heterocycle. We postulate that the dioxime is converted stepwise to the corresponding diimine which process can be formally represented by structures XI to V.



V would then be transformed to the imidazole as previously outlined.[18]

I does not form an imidazole owing to the extraordinary stability of the oxime grouping in this molecule[1] which prevents the conversion to a diketone–dioxime mixture. The monoxime is converted to the monoimine, XIII, a structural type which Stein and Day[19] have converted to the oxazole nucleus, *i.e.*



The dioxime of I has been found to decompose at 100° in benzaldehyde solution, a temperature at which oxazole formation proceeds very slowly, to form a stable isoxazole nitrile.[1] This compound would have been identified readily in the course of isolating II, and the failure to find it is additional evidence that the dioxime is not an intermediate in the conversion of I to II.

(13) G. McCoy and A. R. Day, THIS JOURNAL, **65**, 2159 (1943).

(14) E. A. Steck and A. R. Day, *ibid.*, **65**, 452 (1943).

(15) McCoy and Day, ref. 13, postulate that VII is directly converted into IX, *i.e.*, that the amino group adds across the double bond. We prefer to think of the reaction as involving the addition of the amino group to the keto tautomer VIII.

(16) A. Lapworth, *J. Chem. Soc.*, **91**, 1137 (1907).

(17) G. Ponzio, *Gazz. chim. ital.*, **60**, 429 (1930).

(18) In those syntheses of oxazoles and imidazoles wherein the benzoic acid formed was isolated, the yield of acid was generally equal to or in excess of that required by these equations, or the corresponding one for oxazole formation (*vide infra*), based on the yield of nitrogen heterocycle. Inasmuch as part of the benzoic acid may well have been formed by direct oxidation of benzaldehyde, we do not feel that these data can be used to support the proposed mechanism.

(19) C. W. C. Stein and A. R. Day, THIS JOURNAL, **64**, 2567 (1942).

We have been unable to prepare 5-phenyl-2,3-thiophenequinone-3-oxime[1] to utilize as a precursor for the synthesis of an oxazole isomeric with II.

Experimental[20]

2,5-Diphenylthieno[2,3-*d*]oxazole (II).—A solution of 0.36 g. (1.8 mmoles) of I[1] in 10 ml. of benzaldehyde was refluxed for 18 hours, the benzaldehyde was removed by distillation, and the residue was taken up in chloroform, washed with sodium carbonate solution, and dried. Removal of the solvent left 0.51 g. of a brown solid which was recrystallized from ethanol to give 0.24 g. (48%) of colorless needles, m.p. 175–177°. A sample recrystallized for analysis melted at 176.2–176.8°.

Anal. Calcd. for $C_{17}H_{11}ONS$: C, 73.7; H, 4.0; N, 5.1; S, 11.6. Found: C, 73.4, 74.1; H, 4.1, 4.1; N, 5.2, 5.2; S, 8.7,[20c] 8.9,[20c] 12.2,[20a] 11.3,[21] 11.3,[21] 11.4.[21] The solubility of II in 1:9 acetone:water at 29° is 0.33%.

Ultraviolet spectrum in ethanol: λ_{max} 225 mμ (log ε 3.98); λ_{max} 338 mμ (log ε 4.53); λ_{min} 230 mμ (log ε 3.95); λ_{min} 272 mμ log ε 3.55).

2-(4-Methoxyphenyl)-5-phenylthieno[2,4-*d*]oxazole.—A solution of 1.3 g. (6.3 mmoles) of I in 30 ml. of anisaldehyde was refluxed for three hours. The product was added to 100 ml. of chloroform and extracted with sodium carbonate solution repeatedly until acidification of the alkaline extract no longer gave a precipitate (extraction of these combined precipitates with boiling water left 0.74 g. of recovered I). The dried chloroform solution was distilled to remove the solvent and anisaldehyde, and the residue upon recrystallization from chloroform and then ethanol yielded 0.15 g. (18%) of colorless micro-crystals, m.p. 166.6–166.9°.

Anal. Calcd. for $C_{18}H_{13}O_2NS$: C, 70.4; H, 4.2; N, 4.5; S, 10.4. Found: C, 70.4; H, 4.2; N, 4.6; S, 11.2.

2-(4-Isopropylphenyl)-5-phenylthieno[2,3-*d*]oxazole.—After a solution of 2 g. (9.8 mmoles) of I in 30 ml. of cuminaldehyde[22] was refluxed for eight hours under nitrogen, the excess aldehyde was distilled *in vacuo* and the residue was chromatographed over alumina using carbon tetrachloride as the eluting agent to give 0.27 g. (8%) of an orange solid which after two recrystallizations from ethanol was obtained as colorless needles, m.p. 131.8–132.6°.

Anal. Calcd. for $C_{20}H_{17}ONS$: C, 75.2; H, 5.3; N, 4.4. Found: C, 74.9; H, 5.2; N, 4.7.

2-(*p*-Tolyl)-5-phenylthieno[2,3-*d*]oxazole.—From a solution of 1 g. (5 mmoles) of I in 7 ml. of *p*-tolualdehyde, the oxazole was obtained by the procedure described for the synthesis of the isopropyl analog in a yield of 0.45 g. (30%); m.p. 101.0–102.0°.

Anal. Calcd. for $C_{19}H_{13}ONS$: C, 74.3; H, 4.5; N, 4.7. Found: C, 73.7; H, 4.7; N, 4.9.

Attempted Oxazole Syntheses.—Solutions of I in excess cinnamaldehyde and *n*-hexaldehyde, respectively, were treated as above but afforded only oils which could not be purified; in one run the cinnamaldehyde yielded also a trace of yellow solid, m.p. 173–175°, which was not again isolated.

Oxazole N-Oxides.—The general procedure involved bubbling dry hydrogen chloride into a solution of equimolar quantities of monoxime and benzaldehyde in acetic acid until the solution was saturated with the gas. Precipitation began immediately (except in the reaction with biacetyl monoxime which required the addition of ether) and the product was collected after standing for two days.

Biacetylmonoxime[23] was converted to 2-phenyl-4,5-dimethyloxazole N-oxide hydrochloride in 27% yield; colorless crystals, m.p. 189–191°; lit. m.p. 188°.[9] Benzil monoxime yielded triphenyloxazole N-oxide hydrochloride in 62% yield; upon recrystallization from benzene, the free base was obtained, m.p. 169–172°; lit. m.p. 170–171°.[9] 1,2,3-Cyclohexanetrione-1,3-dioxime was transformed, in 28% yield, into **2-phenyl-7-hydroxyimino-4,5,6,7-tetrahydrobenzoxazole-3-oxide hydrochloride**, m.p. 165–170°; recrystallization from methanol and from petroleum ether yielded the free base, m.p. 130.5–132.0°.

Anal. Calcd. for $C_{13}H_{12}N_2O_3$: C, 64.0; H, 4.9; N, 11.4. Found: C, 64.0; H, 3.9; N, 11.4.

From a mixture of I and benzaldehyde treated as above, the only crystalline product was I recovered in 75% yield. Similarly when I was shaken with excess benzaldehyde and hydrochloric acid for periods of seven hours to three days it was largely recovered unchanged.

1,2,3-Cyclohexanetrione-1,3-dioxime was prepared by adaptation of Semon and Damerell's synthesis of biacetyl monoxime to cyclohexanone; yellow needles, m.p. 205° dec., from methanol; triphenylhydrazone, m.p. 180.0–182.5°, lit. m.p. of dioxime,[24] 200° dec.; triphenylhydrazone, m.p. 182–183°.

Reaction of Biacetyl Monoxime and of 1,2,3-Cyclohexanetrione-1,3-dioxime with Benzaldehyde.—A solution of 10 g. (0.1 mole) of biacetyl monoxime in 30 ml. of benzaldehyde was refluxed for 20 hours. No precipitate had formed after the reaction mixture had stood for six days at 0–5°. The unreacted benzaldehyde and biacetyl monoxime were distilled, and attempts were made to purify the tarry residue by recrystallizing it from various solvents but were unsuccessful.

When 1.0 g. (6 mmoles) of 1,2,3-cyclohexanetrione-1,3-dioxime in 7 ml. of benzaldehyde was refluxed under nitrogen for 18 hours, the oxime decomposed completely. The oxime was recovered largely unchanged when a benzaldehyde solution of it was stirred at room temperature for three days or was refluxed for four hours.

Reaction of Benzil Monoxime with Benzaldehyde.—A solution of 3.0 g. (13 mmoles) of benzil monoxime in 10 g. of benzaldehyde was refluxed for one hour under nitrogen. After distillation of the excess benzaldehyde and of benzoic acid (0.8 g.), 2.0 g. of residue remained which melted at 268–270° after an acetone wash. After recrystallization successively from benzene, aqueous ethanol and acetone the m.p. of the colorless lophine was 273–274°; a mixed m.p. with an authentic sample[11b] showed no depression.

Reaction of Phenanthraquinone Monoxime with Benzaldehyde.—Upon cooling, a solution of 1 g. (4.5 mmoles) of phenanthraquinone monoxime in 7 ml. of benzaldehyde which had refluxed for eight hours deposited 0.5 g. of tan crystals. An ether solution of this material was washed with 15% sodium hydroxide solution followed by water; removal of the solvent left 0.25 g. (19%) of cream colored crystals, m.p. 310–313° from ethanol; picrate, m.p. 280–282°; lit. m.p. for 2-phenylphenanthrimidazole,[14] 312–313°, picrate, m.p. 280°.

The reaction mixture filtrates from this and a duplicate run were combined. Removal of the solvent left a gummy residue which was extracted with ether. The brown, ether-insoluble material, m.p. 196–203°, weighed 0.13 g. and was intractable to further purification. The ethereal extract contained 1.57 g. of gum which yielded 0.2 g., m.p. 146–156°, after two recrystallizations from alcohol; the material was not further investigated.

Attempted Reduction of Benzilam N-Oxide.—One gram (3 mmoles) of benzilam N-oxide and 7 ml. of benzaldehyde were refluxed together for eight hours. Ether was added to the product which was then extracted with dilute hydrochloric acid; and the solvent and excess benzaldehyde were removed *in vacuo*. After extraction of an ethereal solution of the residue with base and distillation of the ether, 0.54 g. of a gummy solid was obtained which melted at 229–230° upon recrystallizations from benzene and from ethanol. This was not benzilam, m.p. 116°, and was not further investigated.

The hydrochloric acid solution was neutralized and extracted with ether whereupon a few mg. of colorless solid was obtained, m.p. 273–274°, from ethanol; mixed m.p. with a sample of lophine showed no depression.

Effect of Added Reagents in Thienoöxazole Synthesis.—Mixtures of 0.50 g. of I, 5.0 ml. of benzaldehyde, and catalytic amounts of hydroquinone, benzoyl peroxide, trichloroacetic acid, dibenzylamine or aluminum chloride were stirred at 150° for two to eight hours. The benzaldehyde

(20) Analyses by (a) W. Mansor, Zürich; (b) Clark Microanalytical Laboratory, Urbana, Ill.; (c) University of Pittsburgh Microanalytical Laboratory.

(21) We are indebted to the Misses Irene Bikulege and Jean Woods of the Gulf Research and Development Laboratories for these sulfur analyses. The fused thiophene–oxazole ring system apparently presents experimental difficulties in the sulfur microanalysis; *cf.*, succeeding analysis.

(22) We wish to thank the Hilton-Davis Company, Cincinnati, Ohio, and Dr. N. Crounse for a gift of this material.

(23) W. L. Semon and V. R. Damerell, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 204.

(24) W. Borsche, *Festschrift Otto Wallach*, 301 (1909).

was removed under reduced pressure, and the residue was dissolved in chloroform, washed with base and then water, and chromatographed; the position of the oxazole band could be determined by its fluorescence under ultraviolet light. No marked differences in yields of oxazole were found; the reproducibility was not of a high order, however. Complete details of these runs are to be found in the thesis of C. M. S.[1]

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE NATIONAL DRUG COMPANY]

Derivatives of 1,4-Benzodioxan. I. 1,4-Benzodioxan-2-carboxamides

BY JOHN KOO, SOUREN AVAKIAN AND GUSTAV J. MARTIN

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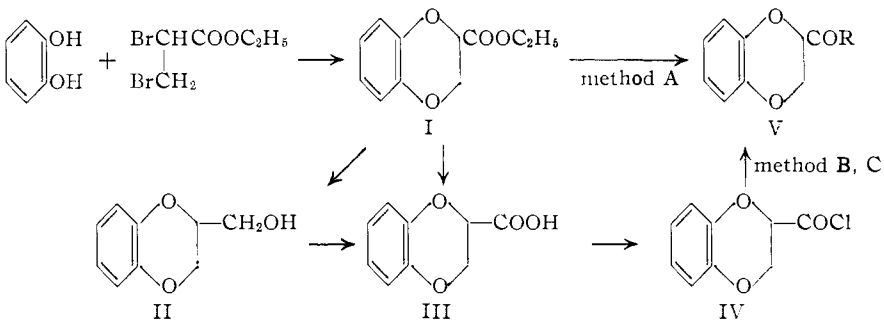
A number of 1,4-benzodioxan-2-carboxamides were synthesized by reaction of ethyl 1,4-benzodioxan-2-carboxylate (I) with primary aliphatic amines or of the corresponding acid chloride IV with secondary, aromatic or heterocyclic amines. The structure of I was proved by reduction to the known 2-hydroxymethyl-1,4-benzodioxan (II), which in turn was oxidized to the acid III.

Relatively little is known about the chemistry and pharmacology of 1,4-benzodioxan derivatives. However, a few N-substituted-2-aminomethyl-1,4-benzodioxans have been used as adrenergic blocking agents,[1] and it was therefore believed desirable to prepare analogous compounds for pharmacological evaluation. This paper describes the synthesis of a number of N-substituted 1,4-benzodioxan-2-carboxamides; they are listed in Table I.

The previously unknown ethyl 1,4-benzodioxan-2-carboxylate (I), considered as a required intermediate, was obtained in good yield by condensation of catechol with ethyl α,β-dibromopropionate in the presence of potassium carbonate. Its structure was proved by lithium aluminum hydride reduction to the known[2] 2-hydroxymethyl-1,4-benzodioxan (II). Permanganate oxidation of II or saponification of I produced the same carboxylic acid III.



R = aliphatic, aromatic or heterocyclic amine

In both instances, the yield of the acid was greatly decreased by employment of slightly stronger conditions such as prolonged heating or more concentrated alkaline solution. It is believed, therefore, that the cyclic ether linkage is more readily cleaved by alkaline reagents in 1,4-benzodioxane than in the somewhat analogous methylenedioxybenzene.

Ammonolysis of the ester I with ammonia, hydrazine or primary aliphatic amines (method A) at room temperature or with slight heating provided the corresponding amides in excellent yield. This method failed, however, with other classes of amines. Secondary amines yielded the desired amides by reaction with the acid chloride IV in boiling methylene chloride (method B). The less reactive aromatic and heterocyclic amines were acylated only in the higher boiling benzene (method C). Finally, 2-aminobenzimidazole was converted to the amide by acylation in pyridine (method D). The reaction product of the ester with 2-amino-1-propanol was acetylated, and the two diastereoisomeric acetyl derivatives were separated.

Experimental[3]

Ethyl 1,4-Benzodioxan-2-carboxylate (I).—To a solution of 77 g. of catechol in 500 ml. of dry acetone was added 70 g. of anhydrous potassium carbonate, then dropwise, with stirring and gentle refluxing, 50 g. of ethyl α,β-dibromopropionate. Another 70 g. of potassium carbonate and 50 g. of dibromo ester was added similarly and this was repeated twice more using altogether 280 g. of potassium carbonate and 200 g. of ester. Stirring and refluxing were continued for another 18 hours, adding periodically dry acetone to keep the reaction mixture fluid enough for stirring. It was then filtered and the residue washed with acetone. Concentrating the filtrate to about 200 ml. and diluting with 300 ml. of cold water precipitated an oil, which was extracted repeatedly with ether. The extracts were washed with water, dried over magnesium sulfate and evaporated. The ester distilled at 105–107° (0.15 mm.) and formed a colorless oil, $n^{25}D$ 1.5214; yield 110 g. (76%).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.65; H, 5.58.

2-Hydroxymethyl-1,4-benzodioxane (II).—To a stirred suspension of 1 g. of lithium aluminum hydride in 100 ml. of anhydrous ether was added 2.0 g. of the ester I in 20 ml. of ether. The mixture was stirred and refluxed for three hours, cooled and decomposed by adding dropwise ice-water, then rapidly 60 ml. of 20% sodium potassium tartrate solution.

(1) E. Fourneau and D. Bovet, *Arch. Intern. pharmacodynamie*, **46**, 178 (1933); M. Goldenberg, C. H. Snyder and H. Aranow, *J. Am. Med. Assoc.*, **135**, 971 (1947).

(2) A. Grun, U. S. Patent 2,366,102 (1944); *C. A.*, **40**, 2271 (1946).

(3) All melting and boiling points are uncorrected. Microanalyses were performed by Mr. S. Alpert and Mr. E. P. McGrady of our Analytical Department.