(ϵ) are assumed to provide an adequate measure of the intensity changes. This statement is not intended to preclude minor changes in band shape on *m*-substitution. However, it may be noted that frequently ϵ_{max} and oscillation strengths are directly related one to another (*cf.* ref. 25).

(25) B. M. Wepster, *Rec. trav. chim.*, **76**, 335 (1957).

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ST. JOHN'S, NEWFOUNDLAND, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

A Novel Ring Closure Involving a Nitro Group; Preparation of Phenanthridine-5-oxide[1]

BY CHESTER W. MUTH, JOHN C. ELLERS AND O. FRED FOLMER

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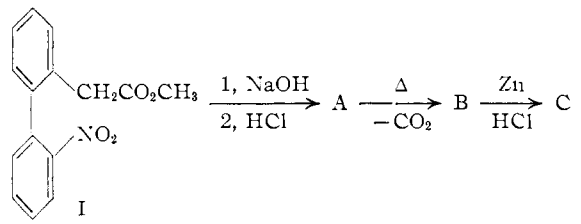
In the biphenyl series a nitro group in the 2-position will react with an activated methylene group in the 2'-position in the presence of sodium hydroxide or sodium methoxide to form substituted phenanthridine-5-oxides. Cyano, carbomethoxy and carbamyl groups are activating groups; hydrogen, hydroxyl, bromo and carboxyl do not serve as activators.

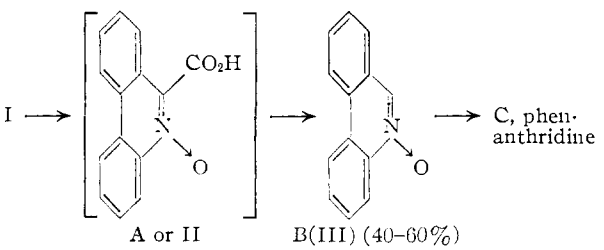
Discussion

An unexpected reaction was observed when methyl 2-(2'-nitrophenyl)-phenylacetate (I)[2] was warmed with methanolic sodium hydroxide in an effort to saponify it. The product obtained was not the parent acid of I, but was compound A, an acid, which had no nitro group and which decomposed with gas evolution to yield compound B. Compound B could be treated with zinc and hydrochloric acid to produce compound C.



I

Compound C was identified as phenanthridine by comparison of its picrate with that of an authentic sample. Compound B was identified as phenanthridine-5-oxide (III) by m.m.p., infrared spectrum and by its picrate. Since the gas given off in the decomposition of compound A was carbon dioxide, the structure postulated for compound A is 6-carboxyphenanthridine-5-oxide (II). With this information the foregoing reactions may be rewritten



A or II B(III) (40–60%)

Since the reaction was very rapid under mild conditions and since the literature did not disclose such a reaction, a further investigation appeared profitable. The further study of this reaction was approached along two lines. First, the reaction of ester I was investigated under a variety of conditions to learn more about the yields, the structure of the acid material and the mechanism of the reaction. Secondly, the carbomethoxy group was replaced by other groups and the resulting compounds were tested for this cyclization.

The bases used which effected the cyclization of ester I were sodium hydroxide in methanol or water and sodium methoxide in methanol. The results are summarized in Table II.

With low base concentration ester I yielded 6-carbomethoxyphenanthridine-5-oxide (IV), whereas ester I with high base concentration and longer reaction time produced acid A and III or acid II and III. Acid A evolved a gas at 120–138° and melted at about 200°, whereas acid II melted at about 200° with no previous gas evolution. Both acids A and II reacted with diazomethane to give the same ester; both yielded phenanthridine-5-oxide when warmed with dimethylformamide and their infrared spectra were nearly identical.

The use of a nitrogen atmosphere[3] or an equal molar quantity of hydroquinone had no effect on the reaction, hence it is assumed that the cyclization is not an oxidation–reduction process. Since the cyclization is not affected by acids (concentrated or dilute sulfuric acids) or by dehydrating agents (acetic anhydride or thionyl chloride) nor by ammonium hydroxide, but only by strong bases (sodium hydroxide and sodium methoxide) it seems likely that the cyclization is a base-catalyzed reaction similar to an aldol condensation.

That hydrolysis of the ester group is not a necessary condition for the cyclization is shown by the production of the cyclized ester, 6-carbomethoxyphenanthridine-5-oxide (IV). This is also shown by the fact that the parent acid, 2-(2'-nitrophenyl)-phenylacetic acid (V), of ester I does not cyclize.

Seven model compounds were subjected to basic conditions to determine whether cyclization would occur. These compounds were the same as methyl 2-(2'-nitrophenyl)-phenylacetate (I) except that the carbomethoxy group was replaced (see V–XI).

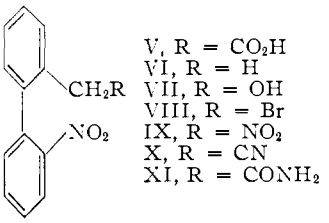
With R as carboxyl (V), hydrogen (VI), hydroxyl (VII) and bromine (VIII) no cyclization

(1) Supported by the National Science Foundation, Research Grant G-1581, whose help we wish to gratefully acknowledge. From the Ph.D. dissertation of O. F. F., 1957, and M.S. thesis of J. C. E., 1958, both from West Virginia University. Presented in part at the 130th Meeting of the A.C.S., Atlantic City, N. J., September, 1956.

(2) C. W. Muth, W. L. Sung and Z. B. Papanastassiou, THIS JOURNAL, **77**, 3393 (1955).

(3) T. Tsuruta, T. Fueno and J. Furukawa, *ibid.*, **77**, 3265 (1955).

occurred under the conditions which caused cyclization of ester I. Qualitative evidence indicated that the compound with R as nitro was prepared. If this is valid then the compound with R as nitro also does not give cyclization.



V, R = CO_2H
VI, R = H
VII, R = OH
VIII, R = Br
IX, R = NO_2
X, R = CN
XI, R = $CONH_2$

With R as cyano (X) or carbamyl (XI) cyclization does take place. Table I shows that the cyano group causes the cyclization to occur more rapidly than does the carbomethoxy group which in turn causes the cyclization to occur more rapidly than does the carbamyl group. This rate order is the same as the order of decreasing *meta*-directing power[4] of the three groups and thus adds credibility to the base-catalyzed type mechanism.

TABLE I

COMPARISON OF CYCLIZATION RATES

	6:1 ratio of base to reactant at 37° in methanol	1:1 ratio of base to reactant in refluxing methanol
Nitrile, X	87% cyclization in 1 min.	.....
Ester, I	8% cyclization 23% recovery after 3 min.	27% cyclization after 9 min.
Amide, XI	.....	88–93% recovery after 10 min.

It is significant that 6-cyanophenanthridine-5-oxide (XII) was obtained in nearly quantitative yields from 2-(2′-nitrophenyl)-phenylacetonitrile (X) at 35° in about 1 minute, whereas X at reflux temperature and with the same base–nitrile ratio and concentration gave little or no cyclized nitrile XII. In the later case the cyclized nitrile XII appeared to form instantaneously and then reacted further as the heating was continued for four minutes.

With R = CN the cyclization reaction is base catalyzed, because with X and a 0.1 *M* quantity of sodium hydroxide the yield of cyclized nitrile XII was 3.5 times that expected assuming the sodium hydroxide and nitrile X are required in a 1:1 ratio.

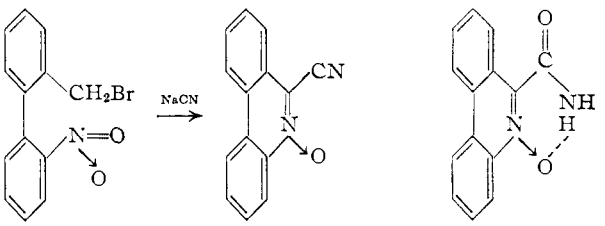
The structure of 6-cyanophenanthridine-5-oxide (XII) was established by elemental analysis, infrared absorption and degradation to phenanthridine-5-oxide (III).

With 2-(2′-nitrophenyl)-phenylacetamide (XI) as shown in Table III and one mole of base no appreciable cyclization occurred in 10 minutes. With the base and amide in a 6:1 ratio approximately the same types and amounts of products were obtained regardless of whether the heating time was 10 minutes or 5.5 hours. However, the longer reaction times gave the better quality products. Cyclized amide XIII and phenanthridine-5-oxide (III) were the only products which could be isolated; it was surprising that no 6-carboxyphenanthridine-5-oxide (II) could be found.

(4) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1956, p. 557.

During attempts at infrared measurements on the amide XI reaction products it was observed that part of the reaction mixture was very insoluble in chloroform. The chloroform-soluble part was phenanthridine-5-oxide. The chloroform-insoluble part was identified as the cyclized amide by its infrared spectrum and by synthesis from the cyclized nitrile XII. The differences in chloroform solubility probably are due to the intrahydrogen bonding in the cyclized amide XIII, whereas the phenanthridine-5-oxide hydrogen bonds with the solvent, chloroform.

It was believed that 2-(2′-nitrophenyl)-benzyl bromide (VIII) could be made to react with sodium cyanide to produce 2-(2′-nitrophenyl)-phenylacetonitrile (X) which would be a model compound and, also, an intermediate for the preparation of ester I. However, as is shown in Table IV the major product was 6-cyanophenanthridine-5-oxide (XII).



VIII XII (50%) XIII

In one run at room temperature a 28% yield of crude 2-(2′-nitrophenyl)-phenylacetonitrile (X) was obtained; however, even in this case the major product was the cyclized nitrile. The explanation must be that the open chain nitrile (X) is being formed in the foregoing reactions and then it cyclizes to form XII because of the base produced by the hydrolysis of the potassium cyanide.[5]

The 2-(2′-nitrophenyl)-phenylbromomethane (VIII) was prepared from the corresponding alcohol, 2-(2′-nitrophenyl)-phenylmethanol (VII), and hydrobromic acid in 79% yield, and the alcohol was prepared from 2-(2′-nitrophenyl)-benzoic acid by way of the acid chloride and subsequent reduction with sodium trimethoxyborohydride in 76% yield.

2-(2′-Nitrophenyl)-phenacetonitrile (X) was prepared in good yields by methods which did not involve any base stronger than ammonium hydroxide. Methyl 2-(2′-nitrophenyl)-phenyl acetate (I) was converted to 2-(2′-nitrophenyl)-phenylacetic acid (V) (91%) by acid hydrolysis and this was in turn converted to the amide XI (72%) by consecutive reactions with thionyl chloride and ammonium hydroxide. The amide XI was dehydrated to the nitrile X (71%) with thionyl chloride.

Four attempts using the method of Kornblum, *et al.*,[6] were made to convert 2-(2′-nitrophenyl)-phenylmethyl bromide (VIII) to 2-(2′-nitrophenyl)-phenylnitromethane (IX). Qualitative tests indicated that IX had been prepared, but it was not obtained pure. The product formed did not cyclize when warmed with methanolic sodium hydroxide.

(5) C. W. Muth, D. O. Steiniger and Z. B. Papanastassiou, THIS JOURNAL, **77**, 1006 (1955).

(6) N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliverto and G. E. Graham, *ibid.*, **78**, 1497 (1956).

Experimental[7]

Methyl 2-(2′-Nitrophenyl)-phenylacetate (I) and Sodium Hydroxide.—The following procedure is typical of those runs listed in Table II in which sodium hydroxide was used except for the differences noted in the table.

TABLE II

REACTION OF METHYL 2-(2′-NITROPHENYL)-PHENYLACETATE (I) WITH BASES

Base	Ratio of base to I	Time, min.	Cyclized ester IV (m.p., °C.), %	Cyclized acid (A) or II and III (m.p., °C.),[a] %	Recovered ester I, %
NaOH	1:1	9	27 (170–174)	.....	..
NaOH	6:1	8[b]	8 (173–176)	.....	23
NaOH	6:1	5	.....	36–57 (214–225)	..
NaOH	6:1	83[c]	.....	41 (210–217)	..
CH_3ONa	1:1	7.2	39 (174–177)	.....	28
CH_3ONa	1:1	10.4	55 (170–176)	<2	<2
CH_3ONa	6:1	25	.....	55 (218–225)	..
CH_3ONa	6:1	23	.....	65 (222–225)	..

[a] The m.p.'s are for III recrystallized at least once from dimethylformamide; the yields are for III based on I; all of II was converted to III. [b] At 37° for 3 min. and 0° for 5 min.; all others were at reflux temp. [c] In water; all others were in methanol.

A solution of 2.0 g. (0.0074 m.) of methyl 2-(2′-nitrophenyl)phenylacetate[8] (I), m.p. 47–48.7°, 1.7 g. (0.042 m.) of sodium hydroxide, and 40 ml. of dry methanol was refluxed on a steam-bath for 5 minutes. The solution formed a gel after heating one minute. The gel was dissolved by adding approximately 20 ml. of water, and the resulting solution was acidified with 12 *N* hydrochloric acid. The solution became bright yellow and a flocculent yellow solid formed. The solid was dried under a stream of air; yield 0.89 g., m.p. 205–215° with some gas evolution at 138°.

The foregoing solid dissolved with vigorous gas evolution when it was warmed with 3 ml. of dimethylformamide. When the solution was cooled a fine white crystalline solid separated which was recrystallized from dimethylformamide; yield 0.46 g., m.p. 221–222°, m.m.p. with authentic phenanthridine-5-oxide 222–224°.

As the filtrate from the foregoing yellow solid was concentrated on a steam-bath more flocculent yellow solid formed. Stirring this solid with 5% sodium hydroxide gave a white solid which was recrystallized from dimethylformamide; yield 0.15 g., m.p. 218–220°, m.m.p. with authentic phenanthridine-5-oxide was 221–224°. The total yield of oxide was 0.61 g. (42.5% based on ester).

Phenanthridine-5-oxide (III).—Ten milliliters of 40% peracetic acid[9] (0.079 atom of active oxygen) in 30 ml. of glacial acetic acid was added to 7.16 g. (0.04 mole) of phenanthridine, m.p. 104–107°, in 60 ml. of chloroform and the mixture was heated on a steam-bath for about 0.5 hour. The unreacted peracetic acid was destroyed by adding an excess of concentrated sodium hydroxide solution. When the chloroform layer was washed with 6 *N* hydrochloric acid *ca.* 6 g. of material, m.p. 180–200° dec., separated. This material was presumably the hydrochloride of III. When dilute sodium hydroxide was added to the foregoing solid, 4.6 g. (59%) of nearly white solid, m.p. 225–228°, was obtained. The analytical sample, nearly white matted crystals, m.p. 226–228° (220°[10]) with little previous sintering, was prepared by two crystallizations from dimethylformamide, one from xylene and finally from a mixture of dimethylformamide and benzene.

Anal. Calcd. for $C_{13}H_9ON$: C, 80.0; H, 4.7; N, 7.2. Found: C, 79.9; H, 4.8; N, 7.2.

The infrared spectrum of III in chloroform showed a strong band at 7.60 μ and three moderately strong bands at 8.65, 8.95 and 9.26 μ, respectively.

The picrate was prepared in chloroform and was found to deteriorate when crystallized from either ethanol or dimethylformamide. The analytical sample, light yellow powder, m.p. 198–200°, was prepared from pure III and it was not recrystallized.

Anal. Calcd. for $C_{19}H_{12}O_8N_4$: C, 53.8; H, 2.9; N, 13.2. Found: C, 53.9; H, 3.0; N, 13.1.

Methyl 2-(2′-Nitrophenyl)-phenylacetate (I) and Sodium Methoxide.—The following procedure is typical of those runs listed in Table II in which sodium methoxide was used except for the differences noted in the Table.

To a boiling solution of sodium methoxide prepared from 0.17 g. (0.0074 gram-atom) of sodium and 5 ml. of methanol was added 2.00 g. (0.0074 mole) of I in 20 ml. of methanol. A nitrogen atmosphere was used throughout the reaction. After 7 min. and 13 sec. (including 5 min. of refluxing), the mixture was cooled with ice and 0.64 ml. of concd. hydrochloric acid was added; a small amount of yellow solid separated. With further standing in an ice-bath and stirring 0.53 g. of white powder, m.p. 174–177° with some previous sintering, separated. The filtrate was cooled with Dry Ice to yield 0.18 g. of nearly white powder, m.p. 168–175°. The total yield of crude 6-carbomethoxyphenanthridine-5-oxide (IV) was 53% based on ester used. The mother liquor was evaporated and residue was leached with ether; 0.14 g. of light brown powder, m.p. 145–155° with small amount of gas evolution, was insoluble in both ether and sodium bicarbonate but soluble in concentrated hydrochloric acid. This latter material was not identified. The ether solution was consecutively washed with 5% sodium bicarbonate, 6 *N* hydrochloric acid, water and saturated sodium chloride solution. Evaporation of the ether gave 0.56 g. (28% recovery of I) of pale yellow solid, m.p. 40–48°; m.m.p. with I did not depress m.p. of product.

6-Carbomethoxyphenanthridine-5-oxide (IV).—In addition to the foregoing method of synthesis for IV, it was prepared by adding an excess of diazomethane to 0.42 g. of A. A white powder was filtered from the reaction mixture; yield 0.27 g., m.p. 168–173° dec. The analytical sample, fluffy white crystals, m.p. 176–178°, was prepared by two recrystallizations from methanol.

Anal. Calcd. for $C_{15}H_{11}O_3N$: C, 71.1; H, 4.4; N, 5.5. Found: C, 71.0; H, 4.2; N, 5.4.

Acid Hydrolysis of Methyl 2-(2′-Nitrophenyl)-phenylacetate (I).—A mixture of 8.0 g. (0.0295 mole) of I and 300 ml. of 6 *N* hydrochloric acid was refluxed for 66 hours. The resulting green, heterogeneous mixture was extracted with ether and the ethereal solution was filtered to remove a small amount of black solid. The ethereal solution was extracted with 5% sodium carbonate and the carbonate solution was acidified to yield a brownish-green oil which soon changed to a green solid; yield 6.51 g. (86%), m.p. 120–121.5°.

The product was identified as 2-(2′-nitrophenyl)-phenylacetic acid by the very close similarity of its infrared spectrum with that of ester I and by analysis of a sample, m.p. 120–121.5°, which was recrystallized from a benzene–petroleum ether (90–100°) mixture.

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.4; H, 4.3; N, 5.4; neut. equiv., 257.2. Found: C, 65.2; H, 4.3; N, 5.5; neut. equiv., 257.2.

6-Carbomethoxyphenanthridine-5-oxide (IV) and Sodium Hydroxide.—A solution of 0.25 g. (*0.000988* mole) of IV, m.p. 175–177°, and 0.877 g. (0.0219 mole) of sodium hydroxide was heated on a steam-bath until maximum gel formation occurred (10 min.). The gel was dissolved in 20 ml. of water and as the solution was acidified with concd. hydrochloric acid 0.213 g. (90%) of fluffy yellow solid (compound A), m.p. 138° with gas evolution, separated.

A duplicate run gave the same results as above except that maximum gel formation occurred in 5 min. In a third run which was stopped after 3 min. the yield of acid II was 36%, and 16% of the starting ester was recovered.

2-(2′-Nitrophenyl)-phenylacetamide (XI).—2-(2′-Nitrophenyl)-phenylacetic acid (7.08 g.) and thionyl chloride (25 ml.) were mixed and allowed to stand overnight before being warmed for an hour on a steam-bath. The excess thionyl chloride was removed under reduced pressure and the residue was poured into 37 ml. of ice-cooled ammonium hydroxide with vigorous stirring to yield 6.88 g. of solid, m.p. 182–193°. Recrystallization from 25 ml. of dimethyl-

(7) All temperatures are uncorrected; all elemental analyses were done by Galbraith Laboratories, Knoxville, Tenn.

(8) Prepared as in reference 2 except that the product was chromatographed on Merck alumina both before and after the final distillation.

(9) We wish to thank the Becco Chemical Division, Food Machinery and Chemical Corp., Buffalo 7, N. Y., for the experimental sample of peracetic acid.

(10) P. Mamalis and V. Petrow, *J. Chem. Soc.*, 703 (1950).

formamide gave 3.93 g. of pale yellow crystals, m.p. 193–195°, and a second crop of 1.18 g., m.p. 192–195°, for total yield of 72%. The analytical sample, m.p. 193–195°, was prepared by recrystallization from dimethylformamide and washing with methanol.

Anal. Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.6; H, 4.7; N, 10.9. Found: C, 65.7; H, 4.7; N, 11.0.

2-(2′-Nitrophenyl)-phenylacetamide (XI) and Sodium Hydroxide.—The following procedure is typical of the runs listed in Table III except for differences in reaction times in some cases. To 0.41 g. (0.01 mole) of sodium hydroxide in 10 ml. of dry methanol, 0.47 g. (0.0018 mole) of XI, m.p. 192–194°, in 12.5 ml. of dry methanol was added. The mixture was refluxed for 5.5 hr. During the latter part of the reflux period, large white coagulations surrounded the boiling stone. This solid was not soluble in dilute hydrochloric acid and no gas was evolved during the acid treatment.

TABLE III

REACTION OF 2-(2′-NITROPHENYL)-PHENYLACETAMIDE (XI) WITH NaOH IN BOILING METHANOL

Time	Cyclized amine (XIII) %	Cyclized amine (XIII) Dec. p., °C.	Phenanthridine-5-oxide (III) %	Phenanthridine-5-oxide (III) M.p., °C.
10 min.	20	250–265	61	170–205[a,b]
2 hr.	28	270–275	50	212–220[a,b]
5.5 hr.	14–21	276–284	38–52	214–221[b]
10 min.[c]	...	.....	...	.....

[a] M.m.p. with authentic material showed no depression of m.p. of reaction product. [b] M.p. of picrate conforms to that of authentic picrate of phenanthridine-5-oxide. [c] In duplicate runs a 1:1 ratio of base to amide gave 90% recovery of XI; in all other runs the ratio of base to amide was 6:1.

The solution was evaporated to dryness by a stream of air and the residue was washed with water. The resulting white powder weighed 0.315 g., m.p. 241–245° with some decomposition. This white powder was leached with 10–15 ml. of boiling chloroform, leaving 0.093 g. (21%) of a white powder, m.p. 279–284° dec. The chloroform solution was evaporated to dryness; yield 0.195 g. (52%) of a white powder, m.p. 214–221.5°, m.p. of picrate 196–198.5°.

The infrared spectrum of the product decomposing at 279–284° was identical with that of authentic 6-carbamylphenanthridine-5-oxide (XIII).

6-Carbamylphenanthridine-5-oxide (XIII).—A solution of 0.42 g. (0.0017 mole) of 6-cyanophenanthridine-5-oxide (XII), m.p. 220–221°, in 10 ml. of concentrated sulfuric acid was allowed to stand at room temperature for about 24 hours. This solution was then placed in a water-bath at 30–45° for several hours, finally being allowed to cool to room temperature overnight. After a total reaction time of 41 hr., the solution was poured onto ice and the light yellow solid which separated was filtered and dried.

The solid was leached with 40 ml. of boiling chloroform and filtered hot. The residue (0.089 g.) was recrystallized from pyridine to yield a white powder, m.p. 285–287 dec., which as used was the analytical sample.

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.6; H, 4.2; N, 11.8. Found: C, 70.4; H, 4.4; N, 11.5.

2-(2′-Nitrophenyl)-phenylmethanol (VII).—To a solution of 1 l. of dioxane containing 40.0 g. (0.151 mole) of 2-(2′-nitrophenyl)-benzoyl chloride[2] was added with vigorous stirring a suspension of 90.0 g. (0.755 mole) of sodium trimethoxyborohydride[11] in 100 ml. of dioxane. The temperature was maintained at 20° during the half-hour addition time; stirring was continued at room temperature for an additional 5 hr. After acidification with hydrochloric acid, the reaction mixture was filtered to remove an inorganic precipitate and steam distilled to remove the dioxane. The residue was extracted three times with 50-ml. portions of benzene. The combined benzene extracts were consecutively washed with water, saturated sodium chloride solution, and filtered through Drierite. Concentration of the benzene extracts yielded 31.9 g. (92%) yellow waxy material, m.p. 73–77°. The analytical sample was prepared by three recrystallizations from benzene to produce a light yellow waxy solid, m.p. 80–82°.

Anal. Calcd. for $C_{13}H_{11}O_3N$: C, 68.1; H, 4.8; N, 6.1. Found: C, 68.2; H, 5.0; N, 6.0.

2-(2′-Nitrophenyl)-phenylbromomethane (VIII).—To 18 ml. of ice-cold hydrogen bromide (48%) solution, 2 ml. of concentrated sulfuric acid was added, and to this solution 2.68 g. (0.0117 mole) of alcohol VII was added carefully in small portions. The addition time was 0.5 hour during which time the reaction temperature was maintained below 5°. The reaction mixture was refluxed for 2 hr., cooled and extracted with benzene. The benzene solution was washed with water, dilute sodium bisulfite solution, saturated sodium chloride solution, filtered through Drierite and concentrated to yield 2.82 g. (82%) of brown crystalline material, m.p. 75–78°. The analytical sample was prepared by three recrystallizations from benzene to produce yellow crystals, m.p. 77–79°.

Anal. Calcd. for $C_{13}H_{10}BrO_2N$: C, 53.4; H, 3.5; Br, 27.4; N, 4.8. Found: C, 53.5; H, 3.5; Br, 27.4; N, 4.6.

6-Cyanophenanthridine-5-oxide (XII).—The following procedure is typical of the experiments summarized in Table IV, except for the differences cited therein and for the isolation of 2-(2′-nitrophenyl)-phenylacetonitrile (X) which will be described later.

TABLE IV

REACTION OF 2-(2′-NITROPHENYL)-PHENYLBROMOMETHANE (VIII) WITH KCN

KCN to VIII ratio	Conditions	Nitrile XII %	Nitrile XII M.p., °C.	Nitrile X %	Nitrile X M.p., °C.
1.20:1	Refl. 2 hr.	44	215–218	...	...
1.40:1	Refl. 2 days	58	206–211	...	...
2.12:1	Refl. 0.5 hr.	64	212–215	...	...
2.12:1	Rm. temp. 1 day	50	219–221	28[a]	62–67

[a] This was proved to be X at least in part because after it was washed with 12 *N* hydrochloric acid and recrystallized from methanol it reacted with methanolic sodium hydroxide to give the same product obtained from authentic X under the same conditions.

To a vigorously stirred solution of 1.07 g. (0.0165 mole) of potassium cyanide dissolved in 30 ml. of ethanol and 15 ml. of water, was added 4.01 g. (0.0137 mole) of bromide VIII during 10 min. The reaction mixture was then stirred for 0.5 hr. at room temperature, refluxed for 2 hr., cooled, and filtered to remove 1.18 g. (37%) of short yellow needles, m.p. 215–218°. The filtrate (A) was extracted three times with 20-ml. portions of benzene. The combined benzene extracts were consecutively washed with water, saturated sodium chloride solution, filtered through Drierite and concentrated to yield 0.250 g. (7%) of short yellow needles, m.p. 218–220°. The analytical sample was recrystallized three times from dimethylformamide to yield short yellow needles, m.p. 220–221°.

Anal. Calcd. for $C_{14}H_8ON_2$: C, 76.3; H, 3.7; N, 12.7. Found: C, 76.2; H, 3.9; N, 12.6.

Degradation of 6-Cyanophenanthridine-5-oxide (XII) to Phenanthridine-5-oxide (III).—To 10 ml. of concentrated sulfuric acid was added 0.27 g. of XII and the solution was allowed to stand overnight. This solution was poured onto ice and a white solid was filtered, washed with water and sodium bicarbonate and finally with water. To 10 ml. of 70–75% sulfuric acid was added 0.16 g. of this new material, m.p. 255–260°, and the resulting mixture was refluxed for 42 hr. The cooled reaction mixture was poured onto ice and as an excess of 50% sodium hydroxide was added a gray precipitate formed which was filtered and washed to yield 0.10 g. of solid, m.p. 221–225°. One recrystallization from dimethylformamide gave 0.065 g. of nearly white powder, m.p. 223–226°. The m.p. of this material was not depressed when it was mixed with authentic oxide III.

2-(2′-Nitrophenyl)-phenylacetonitrile (X).—2-(2′-Nitrophenyl)-phenylacetamide (XI) (4.18 g., 0.0163 mole), m.p. 192–195°, was heated on a steam-bath for 1 hr. with 20 ml. of thionyl chloride. The excess thionyl chloride was removed with partial vacuum and the residue was dissolved in ether. The ether solution was successively washed with

(11) D. C. Iffland and H. Siegel, private communication.

water, dilute sodium carbonate solution and saturated sodium chloride solution before being filtered through Drierite and then concentrated to yield 3.79 g. (97%) of light yellow solid, m.p. 69–74°. After the first recrystallization from methanol the yield was 2.79 g. (71%) of yellow needles, m.p. 71.5–74°. The infrared spectrum indicated that both the cyano and nitro groups were present. The analytical sample, m.p. 72–75°, was prepared by three subsequent crystallizations from methanol.

Anal. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.6; H, 4.2; N, 11.8. Found: C, 70.6; H, 4.4; N, 11.8.

2-(2′-Nitrophenyl)-phenylacetonitrile (X) with Sodium Hydroxide.—In duplicate runs 0.205 g. (0.87 mmole) of X in 0.55 ml. of methanol was mixed with 0.20 g. (5 mmoles) of sodium hydroxide. Twenty-four seconds after the beginning of the addition of the base a yellow precipitate began separating; the temperature had risen from 33 to 38° in about 1 min. After about 8 min. from the time of mixing the precipitate was filtered and washed. The reaction mixture had been kept below room temperature with ice-water about 5 of the 8 min. The yield was 0.166 g. (87%) of yellow crystals, m.p. 218.5–220.5° with no depression in m.m.p. with authentic XII.

In another run duplicating the above except that the reaction mixture was refluxed for 5 min., a yellow precipitate formed instantaneously but it dissolved and no pure XII could be isolated by the above procedure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Rearrangements of α-Halogenated Ethers. I. 2,2,3,3-Tetrachloro-*p*-dioxane

BY R. K. SUMMERBELL AND DANIEL R. BERGER[1]

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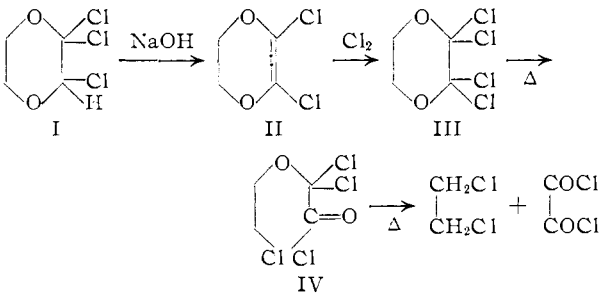
The compound previously assigned the structure 2,2,3,3-tetrachloro-*p*-dioxane (III) has been shown to be (2-chloroethoxy)-dichloroacetyl chloride (IV). III has been synthesized, its structure proved, and the formation of IV from III by a thermal rearrangement has been demonstrated.

Discussion

Some ten years ago the high temperature chlorination of *trans*-2,3-dichloro-*p*-dioxane[2] was described,[3] and the liquid product, obtained in 55% yield, was assigned the structure 2,2,3,3-tetrachloro-*p*-dioxane. This assignment seemed justified as solid derivatives of both ethylene glycol and oxalic acid were isolated from the hydrolysate; no other tetrachlorodioxane could give these derivatives. We recently have had occasion to prepare this compound, and a routine examination of its infrared spectrum revealed a strong absorption at 5.55 μ, entirely inconsistent with its formulation as tetrachlorodioxane.

In order to resolve this inconsistency, the tetrachlorodioxane was prepared by an alternate route. Addition of chlorine to 2-chloro-*p*-dioxene gave 2,2,3-trichloro-*p*-dioxane (I). Removal of hydrogen chloride from I by means of sodium hydroxide gave 2,3-dichloro-*p*-dioxene (II), which upon addition of chlorine gave the desired 2,2,3,3-tetrachloro-*p*-dioxane (III). However, III is entirely different from the previously described liquid, IV. III is a stable white solid melting at 140°, whereas IV is a water-white mobile liquid boiling at 205°. Compound IV reacts "violently" with water and alcohols; III can be recrystallized successfully from aqueous ethanol and is stable to a humid atmosphere. Furthermore, III does not absorb in the region of 5–6 μ.

The structural relationship between III and IV was established as follows: Both gave correct analyses for $C_4H_4O_2Cl_4$, and after hydrolysis both gave derivatives of oxalic acid and ethylene glycol. When III was heated under reflux in tetrachloroethane solution, with the periodic withdrawal of aliquots for spectral examination, the infrared spectrum of III was observed to change slowly to that of IV, the apparently first-order reaction requiring approximately 30 hours for the disappearance of III. Finally, on heating IV at 190° without solvent, there was a very slow distillation, the products being ethylene chloride and oxalyl chloride. On the basis of these observations, the liquid IV is *not* 2,2,3,3-tetrachloro-*p*-dioxane, but rather must be (2-chloroethoxy)-dichloroacetyl chloride. It is entirely possible that in the previously described



preparation of IV[3], III is actually formed as an intermediate. However, the reaction temperature (155°) and the time taken for the reaction (54 hours) are more than are required to permit essentially complete isomerization of III to IV; should any III still be present at the end of the reaction, it would be isomerized in the atmospheric distillation used in the purification scheme for IV. Confirmation of this was obtained by heating III at 210° for 30 minutes. On cooling, the liquid did not solidify, and the infrared spectrum of III was no longer present, having been replaced by that of IV.

The observation that both III and IV could be hydrolyzed to yield derivatives of ethylene glycol requires some comment. Hydrolysis of III would be expected to yield the glycol, whereas the hydrolysis of IV should instead give ethylene chloro-

(1) Northwestern University Fellow, 1955–1956; Allied Chemical and Dye Corp. Fellow, 1956–1957.

(2) See R. K. Summerbell and H. E. Lunk, THIS JOURNAL, **79**, 4802 (1957), for the structures of *cis*- and *trans*-2,3-dichloro-*p*-dioxane.

(3) R. K. Summerbell, R. R. Umhoefer and G. R. Lappin, *ibid.*, **69**, 1352 (1947).