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Diazepines. I. 3,8-Dihalo-11H-dibenzo[c,f]-[1,2]diazepines. (1,2)

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The title compounds were prepared by lithium aluminum hydride reduction of the corresponding 2,2'-dinitro-4,4'-dihalodiphenylmethanes. Peracetic acid oxidation of the title compounds led to the N-oxides, chromic anhydride oxidation led to an 11- keto compound, and hydrazine - Raney nickel reduction led to the dihydro compounds.

In 1906, Duval (4) prepared 3,8-diamino-11*H*-dibenzo[c,f]-[1,2]diazepine-5-oxide (I), by reduction of 2,2'-dinitro-4,4'-diaminodiphenylmethane with zinc dust and ammonium chloride, and subsequent air oxidation in basic medium. I could be reduced with zinc dust and potassium hydroxide to 3,8-diamino-11*H*-dibenzo[c,f]-[1,2]diazepine (II). In connection with the preparation of a model compound for a study of 10-π-electron systems, Allinger and Youngdale (5) prepared the parent compounds III, IV, and V. III was prepared by the deamination of the diazonium salt of I with hypophosphorus acid. Reduction of III with hydrazine and Raney nickel gave 5,6-dihydro-11*H*-dibenzo[c,f]-[1,2]diazepine (V), while reduction with sodium sulfide or with lithium aluminum hydride gave IV. The diazepine IV was also prepared by Theilacker and Korndorfer (6) by lithium aluminum hydride reduction of 2,2'-dinitrodiphenylmethane. These workers reduced IV to V with zinc dust and ammonia in ethanol. More recently, Johns and Markham (7) reported the synthesis of dibenzodiazepinone (VI) by alkaline glucose oxidation of 2,2'-dinitrobenzophenone. Lithium aluminum hydride reduction of 2,2'-dinitrobenzophenone did not lead to compound VI but led to a variety of other products depending upon reaction conditions (7).

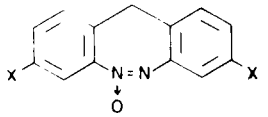
With this background available and with a general interest in diazepines in this laboratory it was decided to study further the 11*H*-dibenzo[c,f]-[1,2]diazepine system. Our initial work, as described in this paper, has been with the 3,8-dihalo series.

The necessary 2,2'-dinitro-4,4'-dihalodiphenylmethanes (VII) were prepared by reactions of the diazonium salt of 2,2'-dinitro-4,4'-diaminodiphenylmethane using standard procedures. It is of interest to note that in the formation of the dibromo compound use of the diazonium sulfate gave considerably higher yields than use of the diazonium bromide. It was also found that cupric bromide could be used in place of cuprous bromide in this reaction although with a substantial decrease in yield. Although such conversions have been reported (8) in the case of *ortho* and *para* nitrodiazonium salts, the nitro groups were *meta* oriented in this case.

The dihalodibenzodiazepine oxides represented by structures VIII, IX, and X were obtained from the appropriate compound VII by the conditions used by Duval (4c) in the preparation of I. As will be discussed later, 3,8-difluoro-11*H*-dibenzo[c,f]-[1,2]-diazepine-5-oxide (XI) was prepared by a different route.

In order to convert the diazepine-N-oxides (VIII-XI) to the parent diazepines (XII-XV), a variety of reducing methods were attempted. Use of Duval's method (4) of converting I to II gave only tarry materials or at best traces of solid when applied to these dihalo compounds. The reduction of IX with sodium sulfide as described (5) for the conversion of III to IV gave only 2,2'-diamino-4,4'-dibromodiphenylmethane. After a number of other negative approaches, it was finally found that the diazepines (XII-XV) could best be prepared by lithium aluminum hydride reduction of the appropriate 2,2'-dinitro-4,4'-dihalodiphenylmethane (VII). In the case of the difluoro and dichloro compounds, this reduction was straightforward, however, in the dibromo example 2,2'-diaminodiphenylmethane was obtained in addition to XIII and in the diiodo instance either XIV or IV could be obtained depending on the ratio of reducing agent to VII. It is of interest to note that this indirect route to the parent diazepine (IV) gave better overall yields and was more convenient than the preparations previously reported (5,6). In general it was found that anhydrous ether gave better yields of the diazepines than did the use of anhydrous tetrahydrofuran, even though the compounds VII were only slightly soluble in ether and they had to be added as a slurry. In connection with the loss of bromine and iodine, it should be noted that Corbett and Halt (9) studied the reduction of a variety of halogenonitroarenes with lithium aluminum hydride and found that chlorine was never eliminated, iodine was always eliminated and that bromine was eliminated when *ortho* to the nitro group. We have, on the other hand, observed loss of a bromine *meta* to a nitro group and retention of iodine under certain conditions.

The oxidation of diazepines XII and XV with peracetic acid gave good yields of the corresponding diazepine-N-oxides (VIII and XI) and this route to the diazepine-N-oxides is much more convenient than the reduction of the 2,2'-dinitro compounds (4).



I X = NH_2

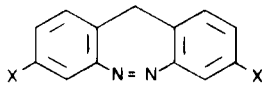
III X = H

VIII X = Cl

IX X = Br

X X = I

XI X = F



II X = NH_2

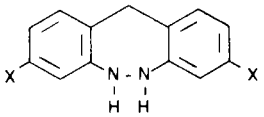
IV X = H

XII X = Cl

XIII X = Br

XIV X = I

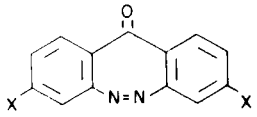
XV X = F



V X = H

XVI X = F

X VII X = Cl



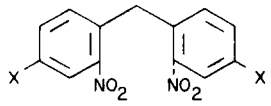
VI X = H

XIX X = Cl

XVIII X = F

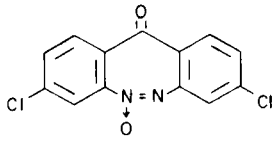
XX X = Br

XXI X = I

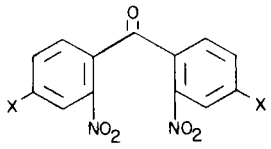


VII

X = NH_2, F, Cl, Br, I



X XII



XXIII

X = halogens

Table I

2, 2'-Dinitro-4, 4'-dihalobenzophenones

Formula	Recryst. Solv.	M.p.	Yield	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
$C_{13}H_6F_2N_2O_5$	acetic acid	151-152	100%	50.66	1.96	9.09	50.85	2.34	9.20
$C_{13}H_6Cl_2N_2O_5$	ethanol	160-162	100%	(reported (12), m.p. 160-162°)					
$C_{13}H_6Br_2N_2O_5$	acetic acid	188	100%	36.30	1.40	6.51	36.12	1.31	6.66
$C_{13}H_6I_2N_2O_5$	ethanol	169-170	57%	29.79	1.15	5.34	29.47	1.31	5.38

Table II

3, 8-Dihalodibenzo[c, f]-[1, 2]diazepin-11-ones

	Formula	Recryst. Solv.	M.p.	Yield	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
XVIII	$C_{13}H_6F_2N_2O$	ethanol	198-199	38	63.93	2.47	11.47	63.78	2.66	11.45
XIX	$C_{13}H_6Cl_2N_2O$	acetic acid	234-235	46	56.34	2.18	10.11	56.11	2.38	9.95
XX	$C_{13}H_6Br_2N_2O$	acetic acid	237-238	64	42.65	1.65	7.65	42.46	1.82	7.92
XXI	$C_{13}H_6I_2N_2O$	ethanol	166-168	59			6.09			5.98

3, 8-Difluoro-5, 6-dihydro-11*H*-dibenzo[c, f]-[1, 2]-diazepine (XVI) and the corresponding dichlorodihydro compound XVII were prepared by the reduction of the corresponding dihalodiazepine with 95% hydrazine and Raney nickel in ether. These compounds were somewhat unstable on standing in air although it was observed that the dichloro compound was considerably less stable than the difluoro compound. Attempts to prepare the dibromo analog gave a white solid which was stable for only a few hours and

could not be analyzed. In the case of the diiodo analog, a colorless product was obtained under reduced pressure but this decomposed immediately on exposure to air. This effect of the halogen on the stability of these dihydrodiazepines is of interest. When the dibromo and diiodo diazepines (XIII and XIV) were refluxed with 95% hydrazine and Raney nickel (rather than just warming) the halogen was lost and 2,2'-diaminodiphenylmethane was the only product of the reaction.

Attempts to reduce 2,2'-dinitro-4,4'-dichlorobenzophenone and 2,2'-dinitro-4,4'-dibromobenzophenone with alkaline glucose, as described for the preparation of VI, failed, and starting material was recovered quantitatively. An attempt to prepare the diazepinone by lithium aluminum hydride reduction of 2,2'-dinitro-4,4'-dichlorobenzophenone led to the isolation of 3,3'-dichloroazobenzene, a product of carbon-carbon fission, and 3,8-dichloro-11*H*-dibenzo[c,f]-[1,2]diazepine, a product of reduction and hydrogenolysis.

In view of these failures to convert the benzophenones to diazepinones, direct conversion of diazepines to the diazepinones was attempted. Selenium dioxide gave only recovered starting material. The 3,8-dihalodibenzo[c,f]-[1,2]diazepin-11-ones (XVIII-XXI) were prepared by oxidation of the corresponding diazepines (XII-XV) with chromic anhydride in glacial acetic acid. That this oxidative procedure leads to the diazepinone ring system was established by oxidizing IV to VI which was identical with a sample kindly supplied by Dr. Johns (7). Use of an excess of chromic anhydride in glacial acetic acid with XII gave 3,8-dichlorodibenzo[c,f]-[1,2]diazepine-11-one-5-oxide (XXII). The structure of this product was proved by oxidation of VIII with chromic anhydride in glacial acetic acid to give a product (XXII) identical with that from XII.

EXPERIMENTAL (10)

2,2'-Dinitro-4,4'-diaminodiphenylmethane (VII, X = NH_2).

Commercially available 4,4'-diaminodiphenylmethane was nitrated with potassium nitrate in sulfuric acid at 0-5° to give an 88% yield of red plates, m.p. 205-206° (reported (4c), m.p. 205-206°).

2,2'-Dinitro-4,4'-difluorodiphenylmethane (VII, X = F).

To a solution of 13 g. of sodium fluoroborate in 20 ml. of concentrated hydrochloric acid and 20 ml. of water at 0° was added with stirring 10 g. (0.034 mole) of 2,2'-dinitro-4,4'-diaminodiphenylmethane. While maintaining the temperature at 10° a solution of 5 g. of sodium nitrate in 10 ml. of water was added dropwise. The mixture was stirred at 0° for 30 min., filtered, and the filtrate washed with a 5% solution of sodium fluoroborate, cold methanol, cold ether, and dried overnight under reduced pressure. A mixture of 10 g. of the 14 g. of diazonium fluoroborate thus obtained and 50 g. of sand was heated with a small flame for 15 min. after the evolution of fumes stopped. The black residue was extracted with ether. Evaporation of the dried ethereal extract gave 1.2 g. (12%) of dark solid which was recrystallized from ethanol to give tan needles, m.p. 98-99°.

Anal. Calcd. for $C_{13}H_8F_2N_2O_4$: C, 53.06; H, 2.74; N, 9.55. Found: C, 52.90; H, 2.79; N, 9.54.

2,2'-Dinitro-4,4'-dichlorodiphenylmethane (VII, X = Cl).

The reaction of the diazonium chloride from 2,2'-dinitro-4,4'-diaminodiphenylmethane with cuprous chloride gave a 55% yield of yellow solid, m.p. 120-121° (reported (11), m.p. 121-122°).

2,2'-Dinitro-4,4'-dibromodiphenylmethane (VII, X = Br).

To a solution of 8.7 g. (0.03 mole) of 2,2'-dinitro-4,4'-diaminodiphenylmethane in 25 g. of glacial acetic acid was added 29.4 g. of concentrated sulfuric acid. To this creamy suspension was added at 0-5° over a 1 hr. period a solution of 2.76 g. of sodium nitrite in 5.4 ml. of water. After stirring for 30 additional min. the solution was added portionwise to a stirred, cooled solution of 14.4 g. of potassium bromide and 6.7 g. of cupric bromide in 45 ml. of water. The mixture was heated at 75° with occasional stirring for 2 hr. and allowed to stand at room temperature for 20 hr. After filtration, the solid was dissolved in benzene and the benzene solution washed with 5% sodium hydroxide and with water. Concentration of the dried benzene solution gave a solid which on recrystallization from ethanol gave 3.2 g. (26%) of yellow crystals, m.p. 136°.

Anal. Calcd. for $C_{13}H_8Br_2N_2O_4$: C, 37.50; H, 1.92; N, 6.73. Found: C, 37.84; H, 2.00; N, 6.55.

Reaction of the diazonium salt formed from 2,2'-dinitro-4,4'-diaminodiphenylmethane and sodium nitrite in sulfuric acid with cuprous bromide in aqueous hydrobromic acid gave a 93% yield of a material identical with that described above.

2,2'-Dinitro-4,4'-diiododiphenylmethane (VII, X = I).

The diazonium sulfate solution from 20 g. (0.07 mole) of 2,2'-dinitro-4,4'-diaminodiphenylmethane and 12 g. of sodium nitrite in 80 ml. of sulfuric acid was allowed to react with urea to destroy the excess nitrous acid and then added to a cold solution of 24 g. of potassium iodide in 30 ml. of water. After standing overnight, the mixture was filtered and the solid recrystallized from ethanol to give 29 g. (85%) of tan needles, m.p. 150-153°.

Anal. Calcd. for $C_{13}H_8I_2N_2O_4$: C, 30.61; H, 1.56; N, 5.49. Found: C, 30.84; H, 1.70; N, 5.71.

3,8-Difluoro-11*H*-dibenzo[c,f]-[1,2]diazepine (XV).

A solution of 1.8 g. (0.006 mole) of 2,2'-dinitro-4,4'-difluorodiphenylmethane in 50 ml. of anhydrous tetrahydrofuran was added dropwise with stirring to a suspension of 2 g. of lithium aluminum hydride in 100 ml. of anhydrous tetrahydrofuran. After 5 hr. at room temperature, water was added and the mixture filtered. Concentration of the dried solvent under reduced pressure gave a gummy residue which was chromatographed over alumina to give 0.5 g. (35%) of yellow needles which were recrystallized from ethanol to give a product, m.p. 184-185°.

Anal. Calcd. for $C_{13}H_8F_2N_2$: C, 67.82; H, 3.50; N, 12.16. Found: C, 67.54; H, 3.63; N, 12.25.

3,8-Dichloro-11*H*-dibenzo[c,f]-[1,2]diazepine (XII).

A slurry of 13 g. (0.039 mole) of 2,2'-dinitro-4,4'-dichlorodiphenylmethane in 300 ml. of anhydrous ether was added slowly with vigorous stirring to 13 g. of lithium aluminum hydride in 200 ml. of anhydrous ether. After 18 hr. at room temperature the mixture was worked up as described above to give after chromatography 7 g. (66%) of solid which was recrystallized from ethanol to give yellow plates, m.p. 204-205°.

Anal. Calcd. for $C_{13}H_8Cl_2N_2$: C, 59.34; H, 3.06; N, 10.65; Cl, 26.95. Found: C, 59.44; H, 3.23; N, 10.65; Cl, 27.18.

3,8-Dibromo-11*H*-dibenzo[c,f]-[1,2]diazepine (XIII).

In a similar manner 5 g. (0.012 mole) of 2,2'-dinitro-4,4'-dibromodiphenylmethane and 1 g. of lithium aluminum hydride in ether gave after chromatography 1.7 g. (40%) of solid which was recrystallized from ethanol to give yellow needles, m.p. 215-216°.

Anal. Calcd. for $C_{13}H_8Br_2N_2$: C, 44.34; H, 2.29; N, 7.95. Found: C, 44.27; H, 2.33; N, 8.24.

Further chromatography gave 0.17 g. (7%) of solid which was recrystallized from petroleum ether - ethyl ether to give white needles of 2,2'-diaminodiphenylmethane, m.p. 134-136° (reported (5), m.p. 134.5-136°).

3,8-Diiodo-11*H*-dibenzo[c,f]-[1,2]diazepine (XIV).

In a similar manner 4.1 g. (0.0082 mole) of 2,2'-dinitro-4,4'-diiododiphenylmethane and 0.6 g. of lithium aluminum hydride in ether gave after chromatography 1.47 g. of starting material and 0.23 g. (25%) of a solid which was recrystallized from ethanol to give yellow crystals, m.p. 244-245°.

Anal. Calcd. for $C_{13}H_8I_2N_2$: C, 35.00; H, 1.80; N, 6.27; I, 56.93. Found: C, 35.11; H, 2.00; N, 6.38; I, 56.95.

11*H*-Dibenzo[c,f]-[1,2]diazepine (IV).

In a similar manner 8 g. (0.015 mole) of 2,2'-dinitro-4,4'-diiododiphenylmethane and 4 g. of lithium aluminum hydride in ether gave after chromatography 1 g. (14%) of solid, m.p. 110-111° (reported (5, 6), m.p. 111.5-112.5°).

3,8-Dichloro-11*H*-dibenzo[c,f]-[1,2]diazepine-5-oxide (VIII).

To a refluxing solution of 7 g. (0.03 mole) of 2,2'-dinitro-4,4'-dichlorodiphenylmethane in 200 ml. of ethanol was added 20 ml. of water and 30 ml. of a 1 N solution of ammonium chloride. The solution was brought to reflux again and 20 g. of zinc dust was added. When the foam became colorless the mixture was filtered rapidly and 80 ml. of ethanol saturated with potassium hydroxide was added. Air was bubbled through the solution for 30 min. and the mixture was filtered and the solid washed with water. Recrystallization from ethanol gave 2.62 g. (29%) of cream colored solid, m.p. 209°.

Anal. Calcd. for $C_{13}H_8Cl_2N_2O$: C, 55.93; H, 2.88; N, 10.03. Found: C, 55.69; H, 2.98; N, 10.22.

This compound was more conveniently prepared by adding 7 ml. of 50% hydrogen peroxide to 0.29 g. (0.0011 mole) of the dichlorodiazepine XII in 15 ml. of glacial acetic acid. The suspension was refluxed for 3 hr. with further additions (5 ml.) of hydrogen peroxide after 30 and 150 min. After standing 18 hr., a solid was filtered and recrystallized from ethanol to give 0.2 g. (63%) of yellow needles, m.p. 209°, which were identical with those obtained from the zinc dust procedure.

3,8-Difluoro-11*H*-dibenzo[c,f]-[1,2]diazepine-5-oxide (XI).

Using the hydrogen peroxide - acetic acid method illustrated above, 0.2 g. (0.0009 mole) of the difluorodiazepine XV gave after recrystallization from ethanol 0.18 g. (82%) of white needles, m.p. 178-180°.

Anal. Calcd. for $C_{13}H_8F_2N_2O$: C, 63.41; H, 3.27; N, 11.37. Found: C, 63.24; H, 3.43; N, 11.41.

3,8-Dibromo-11*H*-dibenzo[c,f]-[1,2]diazepine-5-oxide (IX).

Using the zinc dust procedure illustrated above 1 g. (0.002 mole) of 2,2'-dinitro-4,4'-dibromodiphenylmethane gave after recrystallization from ethanol 0.8 g. (100%) of cream colored crystals, m.p. 219-220°.

Anal. Calcd. for $C_{13}H_8Br_2N_2O$: C, 42.44; H, 2.17; N, 7.60. Found: C, 42.64; H, 2.50; N, 7.81.

3,8-Diiodo-11*H*-dibenzo[c,f]-[1,2]diazepine-5-oxide (X).

Using the zinc dust procedure, 0.7 g. (0.0013 mole) of 2,2'-dinitro-4,4'-diiododiphenylmethane gave after recrystallization from ethanol 0.4 g. (61%) of tan needles, m.p. 226-227°.

Anal. Calcd. for $C_{13}H_8I_2N_2O$: C, 33.79; H, 1.73; N, 6.06. Found: C, 34.19; H, 1.83; N, 6.03.

Reduction of 3,8-Dibromo-11*H*-dibenzo[c,f]-[1,2]diazepine-5-oxide (IX) with Sodium Sulfide.

A mixture of 2 g. (0.0056 mole) of the dibromodiazepine oxide IX and 8 g. of sodium sulfide in 40 ml. of ethanol (80%) was refluxed for 3 hr. After cooling, 0.5 g. of solid was obtained and chromatographed on alumina to give 0.4 g. (18%) of yellow needles which were recrystallized from naphtha to give 2,2'-diamino-4,4'-dibromodiphenylmethane, m.p. 154-155°.

Anal. Calcd. for $C_{13}H_{12}Br_2N_2$: C, 43.85; H, 3.40; N, 7.86. Found: C, 43.74; H, 3.38; N, 8.05.

3,8-Difluoro-5,6-dihydro-11*H*-dibenzo[c,f]-[1,2]diazepine (XVI).

A mixture of 0.2 g. (0.0009 mole) of the difluorodiazepine XV and 1 ml. of 95% hydrazine was dissolved in 20 ml. of warm ether. After the addition of 0.1 g. of Raney nickel the mixture was warmed sufficiently to maintain a vigorous evolution of nitrogen. After 4 hr., the colorless solution was filtered and the solvent evaporated *in vacuo* to give 0.15 g. (66%) of residue which was recrystallized from ether - naphtha to give white needles, m.p. 137-138°.

Anal. Calcd. for $C_{13}H_{10}F_2N_2$: C, 67.23; H, 4.34; N, 12.06. Found: C, 66.99; H, 4.27; N, 12.17.

3,8-Dichloro-5,6-dihydro-11*H*-dibenzo[c,f]-[1,2]diazepine (XVII).

In a similar manner 0.1 g. (0.0003 mole) of the dichlorodiazepine XII gave 0.05 g. (50%) of residue which was recrystallized from ether - naphtha to give white crystals, m.p. 145-146°.

Anal. Calcd. for $C_{13}H_{10}Cl_2N_2$: C, 58.88; H, 3.80; N, 10.56; Cl, 26.83. Found: C, 58.78; H, 3.90; N, 10.62; Cl, 26.58.

To further characterize this product, 0.5 g. (0.0018 mole) was added in portions in 20 ml. methylene chloride to a stirred mixture of 0.5 g. of cinnamylidenemalonyl chloride in 2 ml. of pyridine and 50 ml. of methylene chloride while maintaining the temperature below -50°. The solution was allowed to warm slowly to room temperature and to stand for 3 days. It was washed with dilute hydrochloric acid, dried (sodium sulfate), and evaporated under reduced pressure to give a residue which was chromatographed over alumina to yield 0.74 g. (88%) of yellow solid. Recrystallization from ethanol gave yellow crystals, m.p. 188-190°.

Anal. Calcd. for $C_{25}H_{16}Cl_2N_2O_2$: C, 67.12; H, 3.60; N, 6.26; Cl, 15.85. Found: C, 66.84; H, 3.78; N, 6.54; Cl, 16.11.

2,2'-Dinitro-4,4'-dihalobenzophenone (XXIII).

In a typical preparation, a solution of 0.0016 mole of the dinitrodihalodiphenylmethane in 20 ml. of glacial acetic acid was heated to reflux and 1.5 g. of chromic anhydride was added slowly. The mixture was refluxed for 2 hr., cooled, and water added. The solid obtained was then recrystallized from an appropriate solvent. The products are collected in Table I.

Reduction of 2,2'-Dinitro-4,4'-dichlorobenzophenone (XXIII, X = Cl) with Lithium Aluminum Hydride.

To a mixture of 6 g. of lithium aluminum hydride in 100 ml. of tetrahydrofuran was added a solution of 4.5 g. (0.013 mole) of 2,2'-dinitro-4,4'-dichlorobenzophenone in 50 ml. of tetrahydrofuran with stirring. After 19 hr., water was added and the mixture filtered. Concentration of the dried (magnesium sulfate) filtrate gave a residue which was chromatographed over alumina to give two components. Obtained first was 0.32 g. (10%) of a solid m.p. 95-96° (reported (13), m.p. 101° for 3,3'-dichloroazobenzene).

Anal. Calcd. for $C_{12}H_8Cl_2N_2$: N, 11.24. Found: N, 11.05.

In a second fraction was obtained a small amount of yellow solid, m.p. 205-206°, which was identical with an authentic sample of 3,8-dichloro-11*H*-dibenzo[c,f]-[1,2]diazepine (XII).

3,8-Dihalodibenzo[c,f]-[1,2]diazepin-11-one (XVIII-XXI).

In a typical preparation, a mixture of 0.0018 mole of the dihalodiazepine, 0.8 g. of chromic anhydride, and 15 ml. of glacial acetic acid was refluxed for 15-60 min. and poured into water to give a solid which was recrystallized from an appropriate solvent. These products are included in Table II.

Dibenzo[c,f]-[1,2]diazepin-11-one (VI).

In a similar manner 1 g. (0.0005 mole) of the parent diazepine IV was oxidized with 0.5 g. of chromic anhydride in glacial acetic acid to give 0.05 g. (40%) of orange needles, m.p. 193° (reported (7), m.p. 197°). The infrared and ultraviolet spectra of this product were identical to those of an authentic sample (14).

3,8-Dichlorodibenzo[c,f]-[1,2]diazepine-5-oxide-11-one (XXII).

In a similar manner, oxidation of 0.3 g. (0.0011 mole) of the dichlorodiazepine XII with 1 g. of chromic anhydride in glacial acetic acid gave 0.15 g. (40%) of solid which was recrystallized from glacial acetic acid to give yellow needles, m.p. 254-255°.

Anal. Calcd. for $C_{13}H_6Cl_2N_2O_2$: C, 53.26; H, 2.06; N, 9.55; Cl, 24.09. Found: C, 53.58; H, 2.36; N, 9.80; Cl, 24.02.

In a similar manner, 0.08 g. (0.00027 mole) of the dichlorodiazepine-N-oxide VIII and 0.4 g. of chromic anhydride in glacial acetic acid gave 0.03 g. (33%) of yellow needles, m.p. 253-254°, which were identical with those from XII.

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