

Diazepines. IV. Oxidative Cyclizations (1)

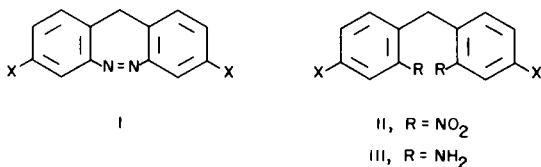
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Dibenzo[*c,f*][1,2]diazepines (I) have been prepared from 2,2'-dinitrodiphenylmethanes (II) by reductive methods (2). We have now found that these compounds can also be prepared from 2,2'-diaminodiphenylmethanes (III) by oxidative methods.

Pausacker (3) has noted the use of iodosobenzene diacetate to oxidize aromatic amines to azobenzenes. When 2,2'-diaminodiphenylmethane (III, X = H) and 2,2'-diamino-4,4'-dichlorodiphenylmethane (III, X = Cl) were oxidized by iodosobenzene diacetate the desired diazepines (I, X = H and I, X = Cl, respectively) were obtained. No 3,8-dichlorodibenzo[*c,f*][1,2]diazepine-11-one, however, could be isolated when 2,2'-diamino-4,4'-dichlorobenzophenone was treated with iodosobenzene diacetate.

Prior to the use of iodosobenzene diacetate an attempt was made to use the procedure which Payne (4) used to convert aniline to azoxybenzene. Treatment of 2,2'-diamino-4,4'-dichlorobenzophenone under Payne's conditions (acetonitrile and hydrogen peroxide at pH 8) gave 2-nitro-2'-amino-4,4'-dichlorobenzophenone rather than any diazepinone. Compound III (X = Cl) failed to give any diazepine under Payne's conditions.



EXPERIMENTAL

2,2'-Diaminodiphenylmethane.

To 500 ml. of ethanol containing 5 g. of 2,2'-dinitro-4,4'-diiododiphenylmethane (5) and 5 g. of 5% palladium on charcoal was added dropwise 100 ml. of 95% hydrazine. The mixture was refluxed for 24 hours, filtered and evaporated to give a 77% yield of 2,2'-diaminodiphenylmethane (III, X = H) (6).

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

A mixture of 0.5 g. of 2,2'-diaminodiphenylmethane and 1.1 g. of iodosobenzene diacetate (7) in 70 ml. of anhydrous benzene was stirred at room temperature for 3 days. The mixture was filtered and the filtrate was concentrated to a gum which was purified by dry column chromatography on alumina in benzene. The diazepine was obtained in 50% yield from this chromatography and was identical in all respects to an authentic sample (5).

2,2'-Diamino-4,4'-dichlorodiphenylmethane.

This compound (8) was obtained in 76% yield by reduction of 2,2'-dinitro-4,4'-dichlorodiphenylmethane (5) with iron and glacial acetic acid.

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

A mixture of 0.32 g. of 2,2'-diamino-4,4'-dichlorodiphenylmethane and 0.55 g. of iodosobenzene diacetate in 50 ml. of benzene were treated as described above to give a 35% yield of diazepine identical in all respects with an authentic sample (5).

2,2'-Diamino-4,4'-dichlorobenzophenone.

This compound (9) was obtained in 65% yield by reduction of 2,2'-dinitro-4,4'-dichlorobenzophenone (5) with iron and acetic acid.

Oxidation of 2,2'-Diamino-4,4'-dichlorobenzophenone.

To a stirred solution of 0.84 g. of the benzophenone and 41 g. of acetonitrile in 300 ml. of methanol on the steam bath was added 41 g. of 50% hydrogen peroxide over a 1-hour period. The pH of the solution was maintained at 8 by addition of sodium hydroxide solution. The mixture was stirred under reflux for 2 hours, cooled, and 5% palladium on charcoal added. After standing overnight in the cold, the mixture was filtered and concentrated until a solid began to appear. The mixture was extracted with chloroform and the dried extracts were concentrated to give a solid which after chromatography and recrystallization from ethanol-water was obtained in 30% yield, m.p. 125-127°. Infrared (potassium bromide); 3300, 3200, 1620, 1520, 1330 cm⁻¹.

Anal. Calcd. for C₁₃H₈Cl₂N₂O₃: C, 50.18; H, 2.59; N, 9.00; Cl, 22.79. Found: C, 50.07; H, 2.53; N, 8.92; Cl, 22.30.

Acetamide was also isolated from the chromatography of the crude reaction product.

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