272. *Proximity Effects in Diaryl Derivatives. Part I. The Formation of Seven-membered Heterocyclic Compounds.*

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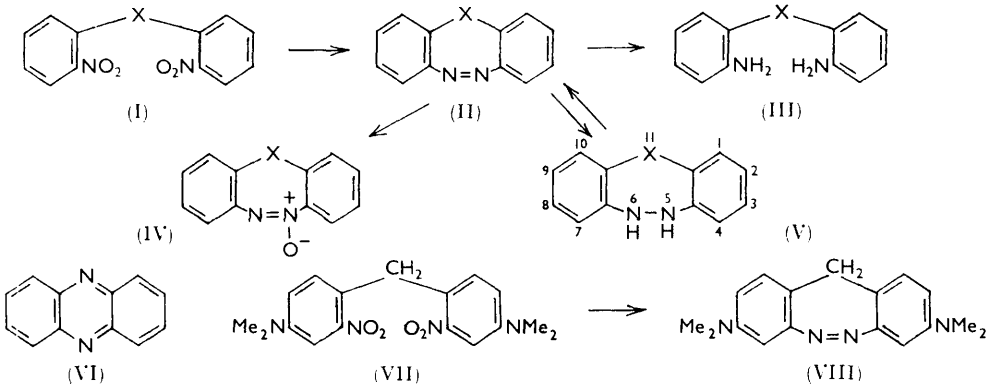
Dibenz[1,4,5]oxadiazepine has been prepared from 2,2′-dinitrodiphenyl ether, and converted into its *N*-oxide and 5,6-dihydro-derivative. Reduction of 2,2′-dinitrodiphenylamine affords a mixture of dibenzo[1,4,5]triazepine and its *N*-oxide.

Heterocyclic syntheses provide many examples of unusual reactions arising from the proximity of substituents in aromatic rings. For example, Loudon and his collaborators [1] showed that quinoline and indole derivatives are formed readily by interaction of aromatic nitro-groups and *ortho*-side-chains. In contrast, displacement of an *ortho*-substituent frequently occurs when a diaryl derivative containing two *ortho*-nitro-groups (I) is reduced in alkaline solution. 2,2′-Dinitrodiphenylamines (I; X = NH), for example, are converted into phenazines (VI) by sodium sulphide,[2] and into dihydrophenazines when sodium methoxide is the reducing agent.[3] Similarly, phenothiazines are obtained from the reaction of hydrazine with 2,2′-dinitrodiphenyl sulphides (I; X = S).[4] Reduction of 2,2′-dinitro-compounds (I) with acidic reagents usually affords the corresponding diamines (III),[5,6] but there are some instances of the isolation of heterocyclic compounds from these reactions. Thus, 2,2′,4,4′-tetranitrobenzophenone was converted into an acridone by stannous chloride and hydrochloric acid,[7] and Matsumura obtained a diaminophenazine in 7% yield on reduction of 2,2′,4,4′-tetranitrodiphenyl ether with the same reagents,[8] the latter reaction involving rearrangement as well as displacement of an *ortho*-substituent. Our studies, which are concerned with the reduction of 2,2′-dinitrodiphenyl ethers and 2,2′-dinitrodiphenylamines, are designed to clarify the mechanisms of some of these cyclisations.

[1] Loudon and Wellings, *J.*, 1960, 3462, 3470; Loudon and Tennant, *ibid.*, p. 3466.
[2] Coker, Plant, and Turner, *J.*, 1951, 110.
[3] Rozum, *Ukrain. khim. Zhur.*, 1950, **16**, No. 4, 434 (*Chem. Abs.*, 1955, **49**, 1063).
[4] Farrington, *Austral. J. Chem.*, 1959, **12**, 196.
[5] Tomlinson, *J.*, 1939, 158.
[6] Haussermann and Bauer, *Ber.*, 1897, **30**, 738.
[7] Schöpff, *Ber.*, 1894, **27**, 2316.
[8] Matsumura, *J. Amer. Chem. Soc.*, 1930, **52**, 3199.

In the reduction of dinitro-compounds (I) under alkaline conditions, cyclisation to diazepines (II) might be expected to compete with the displacements discussed above. Indeed, structure (VIII) was assigned to the product of the reaction of the diphenylmethane derivative (VII) with zinc and sodium hydroxide.[9] We have now prepared



dibenz[1,4,5]oxadiazepine (II; X = O) and dibenzo[1,4,5]triazepine (II; X = NH) in order to study the role of diazepines in the reduction of dinitro-compounds (I).

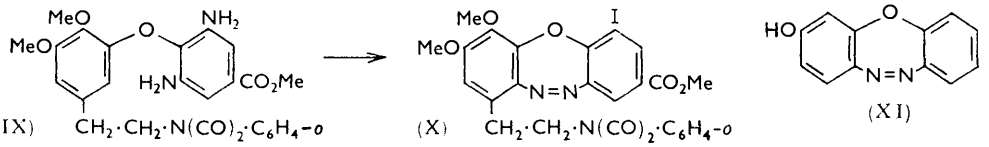
Lithium aluminium hydride is an efficient reagent for the conversion of aryl nitro-compounds into azo-derivatives,[10] and for the corresponding intramolecular reaction whereby benzocinnolines are prepared from 2,2′-dinitrobiphenyls.[11] When 2,2′-dinitrodiphenyl ether was treated with lithium aluminium hydride a similar reaction occurred, and the orange crystalline dibenz[1,4,5]oxadiazepine (II; X = O) was obtained in 23—25% yield. The compound was isolated either by chromatography or by distillation. The conjugated system in dibenz[1,4,5]oxadiazepine is revealed by the ultraviolet absorption maximum at 310 mμ (log ε 3·75). The non-planar nature of the ring system is presumably responsible for the rather low intensity of this band [cf. *cis*-azobenzene, $\lambda_{max.}$ 324 mμ (log ε 4·18) and *trans*-azobenzene, $\lambda_{max.}$ 319 mμ (log ε 4·29) [12]].

The structure of the oxadiazepine was confirmed by the following reduction and oxidation experiments. Catalytic hydrogenation, involving the absorption of 2 mol. of hydrogen, afforded 2,2′-diaminodiphenyl ether (III; X = O). Reduction of the oxadiazepine with lithium aluminium hydride or with zinc and sodium hydroxide gave a good yield of 5,6-dihydrodibenz[1,4,5]oxadiazepine (V; X = O). In accord with this structure, the compound was colourless and did not have an ultraviolet absorption maximum above 280 mμ; it absorbed in the infrared region at 3300 and 3180 cm.$^{-1}$ (NH). The dihydro-compound was oxidised to dibenz[1,4,5]oxadiazepine, slowly by air and rapidly by bromine in alkaline solution. It dissolved in hydrochloric acid and was precipitated from acid solution by alkali. Dibenz[1,4,5]oxadiazepine (II; X = O) was converted by peracetic acid into its orange crystalline 5-oxide (IV; X = O), reaction of which with lithium aluminium hydride or with zinc and sodium hydroxide gave the same dihydro-compound (V; X = O) as was prepared by reduction of the oxadiazepine.

The first dibenz[1,4,5]oxadiazepine (X) to be reported was obtained by Crowder, Grundon, and Lewis [13] by an azo-coupling reaction involving the tetrazonium salt derived from amine (IX). This method is not suitable for the synthesis of the parent compound (II; X = O), but Allinger and Youngdale [14] recently prepared the monosubstituted

[9] Duval, *Compt. rend.*, 1909, **149**, 401.
[10] Nystrom and Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738.
[11] Badger, Seidler, and Thomson, *J.*, 1951, 3207.
[12] Cook, Jones, and Polya, *J.*, 1939, 1315.
[13] Crowder, Grundon, and Lewis, *J.*, 1958, 2142.
[14] Allinger and Youngdale, *J. Amer. Chem. Soc.*, 1962, **84**, 1020.

oxadiazepine (XI) by an analogous reaction; these authors also obtained dibenz[1,4,5]-oxadiazepine (II; X = O) and its dihydro-derivative (V; X = O) by procedures similar to those described in this paper.



Reduction of 2,2′-dinitrodiphenylamine (I; X = NH) with zinc and sodium hydroxide in aqueous dioxan at 20° gave a mixture of red crystalline compounds, separated by chromatography into dibenzo[1,4,5]triazepine (II; X = NH) (20%) and its *N*-oxide (IV; X = NH) (13%). The yields of both products are dependent on the amount of alkali employed (see Experimental).

Dibenzo[1,4,5]triazepine has an ultraviolet spectrum similar to that of dibenz[1,4,5]-oxadiazepine, and some of the reactions of the two compounds are also analogous. Thus, oxidation of the triazepine with peracetic acid afforded the *N*-oxide (IV; X = NH). In the presence of a palladium catalyst, the triazepine rapidly absorbed 2 mol. of hydrogen with the formation of 2,2′-diaminodiphenylamine (III; X = NH), characterised as its diacetyl derivative. Reduction of the triazepine with hydrazine and Raney nickel or with zinc and sodium hydroxide furnished a colourless compound which was not 2,2′-diamino-diphenylamine; this product showed three peaks in the NH region of the infrared spectrum, and is therefore probably 5,6-dihydrodibenzo[1,4,5]triazepine (V; X = NH). The compound could not be purified, since oxidation by air to the red triazepine (II; X = NH) occurred very rapidly.

Reduction of 2,2′-dinitrodiphenylamine with lithium aluminium hydride or with sodium arsenite did not give dibenz[1,4,5]triazepine or its derivatives. In the reaction with sodium arsenite (a reagent used for the preparation of azoxybenzene from nitrobenzene [15]) phenazine (VI) was formed in 34% yield. Surprisingly, phenazine (2%) was also isolated from the reduction of 2,2′-dinitrodiphenyl ether with lithium aluminium hydride. An investigation of the formation of phenazine in these two reactions is in progress.

Experimental

2,2′-Dinitrodiphenyl Ether.—Heating potassium *o*-nitrophenoxide with *o*-chloronitrobenzene at 230—240° for 4 hr.[6,16] gave 2,2′-dinitrodiphenyl ether, m. p. 114—115°, in 65% yield, but a violent reaction sometimes occurred (as observed previously [17]), resulting in a considerably lower yield.

Dibenz[1,4,5]oxadiazepine (II; X = O).—(*a*) A solution of 2,2′-dinitrodiphenyl ether (15 g.) in tetrahydrofuran (150 c.c.) was added slowly to lithium aluminium hydride (12 g.) in tetrahydrofuran, and the solution was kept at room temperature for 12 hr. After decomposition of the excess of the reagent with water, the mixture was filtered, concentrated under reduced pressure, and extracted with ether (500 c.c.). The ether solution was shaken with 5% aqueous sodium carbonate and evaporated. The residue in benzene (100 c.c.) was chromatographed on alumina. Elution with benzene gave dibenz[1,4,5]oxadiazepine as a red oil, separating from light petroleum (b. p. 40—60°) in orange needles (2·25 g., 23%), m. p. 48—50°, raised by crystallisation from the same solvent to 56—57° (lit.,[14] 57·5—58·5°), $\lambda_{max.}$ 250 (log ε 4·30), 268 (log ε 3·75), and 310 mμ (log ε 3·75) (Found: C, 73·3; H, 4·4; N, 14·7. Calc. for $C_{12}H_8N_2O$: C, 73·4; H, 4·1; N, 14·3%).

In a second experiment, the crude product was distilled at 0·1 mm. The sublimate obtained at 60—65° separated from benzene in yellow needles (0·2 g., 2%), m. p. 174—176°, identical

[15] Bigelow and Palmer, *Org. Synth.*, Coll. Vol. II, p. 57.
[16] Haussermann and Bauer, *Ber.*, 1896, **29**, 2083.
[17] Cullinane, Davey, and Padfield, *J.*, 1934, 716.

(mixed m. p. and infrared) with authentic phenazine. The dibenz[1,4,5]oxadiazepine distilled at 110—115°, and crystallised from light petroleum (b. p. 40—60°) in orange needles (2·45 g., 25%), m. p. 47—50°.

(*b*) A solution of bromine (0·5 c.c.) in 10% aqueous sodium hydroxide (10 c.c.) was added to 5,6-dihydrodibenz[1,4,5]oxadiazepine (1 g.), in ether (10 c.c.), and the mixture was shaken for 12 hr. The ether layer was washed with water and evaporated. Crystallisation of the residue from light petroleum (b. p. 40—60°) gave dibenz[1,4,5]oxadiazepine in orange needles (0·5 g., 51%), m. p. 56—57° alone or mixed with a sample obtained as in (*a*).

Catalytic Reduction of Dibenz[1,4,5]*oxadiazepine.*—Dibenz[1,4,5]oxadiazepine (0·45 g.) in ethanol (25 c.c.) was hydrogenated at room temperature and atmospheric pressure in the presence of platinum. After removal of the catalyst, the solvent was evaporated. Crystallisation of the residue from aqueous ethanol gave 2,2′-diaminodiphenyl ether in needles (0·3 g., 71%), m. p. 60—61°, identical (mixed m. p. and infrared spectra) with a sample, m. p. 60—61°, prepared by reduction of 2,2′-dinitrodiphenyl ether.[6]

Dibenz[1,4,5]*oxadiazepine 5-Oxide* (IV; X = O).—A solution of dibenz[1,4,5]oxadiazepine (0·3 g.) in acetic acid (20 c.c.) and 10% hydrogen peroxide (10 c.c.) was heated at 100° for 4 hr. Addition of water (100 c.c.) and extraction with ether gave *dibenz*[1,4,5]*oxadiazepine 5-oxide*, crystallising from light petroleum (b. p. 60—80°) in orange needles (0·18 g., 56%), m. p. 80—81° (Found: C, 67·6; H, 3·9; N, 13·1. $C_{12}H_8N_2O_2$ requires C, 67·9; H, 3·8; N, 13·2%).

5,6-*Dihydrodibenz*[1,4,5]*oxadiazepine* (V; X = O).—Zinc powder (1 g.) was added in portions to a solution of dibenz[1,4,5]oxadiazepine (0·2 g.) in ethanol (20 c.c.) and 10% aqueous sodium hydroxide (10 c.c.), and the mixture was stirred at 20° for 12 hr. After filtration, the solution was concentrated to remove ethanol and extracted with ether. Evaporation of the ether gave 5,6-dihydrodibenz[1,4,5]oxadiazepine, separating from aqueous ethanol in needles (0·15 g., 75%), m. p. 100—101° (lit.,[14] 98·5—99°) (Found: C, 72·5; H, 5·1; N, 14·4. Calc. for $C_{12}H_{10}N_2O$: C, 72·7; H, 5·1; N, 14·3%). The product dissolved in hydrochloric acid and was precipitated from the acid solution by addition of an excess of aqueous sodium hydroxide.

(*b*) Dibenz[1,4,5]oxadiazepine (0·14 g.) in dry ether was added slowly to lithium aluminium hydride (1 g.) in dry ether (25 c.c.), and the solution was stirred at 20° for 1 hr. Addition of water, filtration, evaporation of the ether solution, and crystallisation of the residue from light petroleum (b. p. 80—100°) gave 5,6-dihydrodibenz[1,4,5]oxadiazepine in needles (0·1 g., 71%), m. p. 100—101°, identical with a sample prepared as in (*a*).

(*c*) Reduction of dibenz[1,4,5]oxadiazepine 5-oxide (0·1 g.) with zinc and sodium hydroxide for 2 hr. as described in (*a*) gave 5,6-dihydrodibenz[1,4,5]oxadiazepine (0·06 g., 64%), m. p. 100—101°.

The dihydro-compound (0·15 g., 40%) was also obtained from the *N*-oxide (0·4 g.) by reduction with lithium aluminium hydride by method (*b*).

Dibenzo[1,4,5]*triazepine* (II; X = NH) *and its 5-Oxide* (IV; X = NH).—A solution of 2,2′-dinitrodiphenylamine [18] (10 g.) in dioxan (1250 c.c.) and 40% aqueous sodium hydroxide (100 c.c., 25 mol.) was treated with portions of zinc powder (total, 20 g.) during 2 hr. After a further 20 hr., the mixture was filtered. The filtrate was concentrated to 300 c.c., diluted with water (1500 c.c.), and extracted with methylene chloride (12 times). The residue obtained by evaporation of the methylene chloride solution was extracted with benzene (100 c.c.) and the benzene solution was chromatographed on alumina (300 g.). Elution with benzene gave no crystalline compounds, but subsequent elution with benzene–chloroform (4 : 1) gave a red semi-crystalline product which was again chromatographed on alumina (65 g.). Elution with benzene–chloroform (4 : 1) gave two fractions.

Evaporation of the first fraction, and crystallisation of the residue from benzene, gave *dibenzo*[1,4,5]*triazepine* in red needles (1·3 g., 20%), m. p. 188—189°, raised by recrystallisation to 191°, $\lambda_{max.}$ 247 mμ (log ε 4·25), 305 mμ (log ε 3·88), $\nu_{max.}$ 3300 cm.$^{-1}$ (NH) (Found: C, 73·2; H, 4·5; N, 21·0. $C_{12}H_9N_3$ requires C, 73·8; H, 4·7; N, 21·5%). Evaporation of the second fraction and trituration of the residue with benzene gave *dibenzo*[1,4,5]*triazepine 5-oxide* as a red solid (1·05 g., 13%), separating from benzene in red needles, m. p. 199°, $\nu_{max.}$ 3300 cm.$^{-1}$ (NH) (Found: C, 68·1; H, 4·5; N, 20·2. $C_{12}H_9N_3O$ requires C, 68·2; H, 4·3; N, 19·9%).

When 12·5 mol. of sodium hydroxide were used in the preparation, a mixture of the triazepine (3%) and the oxide (10%) was obtained. When 50 mol. of sodium hydroxide were employed, the triazepine was isolated in 13% yield, but the oxide was not detected.

[18] Eckert and Steiner, *Monatsh.*, 1914, **35**, 1153.

Oxidation of Dibenzo[1,4,5]*triazepine.*—A solution of dibenzo[1,4,5]triazepine (110 mg.) in acetic acid (25 c.c.) containing 30% hydrogen peroxide (2·5 c.c.) was kept at room temperature for 12 hr. Dilution with water, neutralisation with sodium carbonate, extraction with methylene chloride, and evaporation of the extract gave a red residue, which was chromatographed on alumina. Elution with benzene gave unchanged triazepine (14 mg.). Elution with benzene–ether (9 : 1), evaporation of the solvent, and crystallisation of the residue from benzene afforded dibenzo[1,4,5]triazepine 5-oxide (83 mg., 73%), m. p. 195—197°, identical (mixed m. p. and infrared spectra) with an authentic sample.

Reduction of Dibenzo[1,4,5]*triazepine.*—(*a*) A solution of dibenzo[1,4,5]triazepine (224 mg.) in methanol (25 c.c.) was hydrogenated at room temperature and atmospheric pressure in the presence of palladium (10% on charcoal). Absorption of 2 mol. of hydrogen was complete in 7 min. After filtration, the solution was evaporated to give 2,2′-diaminodiphenylamine as a solid (216 mg., 92%), which rapidly discoloured. The compound had m. p. 86—90°, undepressed on admixture with an authentic sample, m. p. 98—99° (lit.,[5] m. p. 101°), but not altered by repeated crystallisation from light petroleum (b. p. 60—80°). Treatment of the product with acetic anhydride gave the diacetyl derivative, separating from benzene in needles, m. p. 197—199°, identical (mixed m. p. and infrared spectra) with an authentic sample, m. p. 199—200° (lit.,[5] m. p. 199°).

(*b*) Reduction of dibenzo[1,4,5]triazepine with hydrazine and Raney nickel and crystallisation of the product from ethanol furnished colourless prisms, m. p. 95—115°, $\nu_{max.}$ 3300, 3280, and 3200 cm.$^{-1}$, which rapidly became red. The reduction was also carried out with zinc and sodium hydroxide; during isolation, the initially colourless product became red, and the triazepine, m. p. 190—191°, was obtained.

Reduction of 2,2′-Dinitrodiphenylamine with Sodium Arsenite.—2,2′-Dinitrodiphenylamine (1·25 g.), arsenious oxide (1·5 g.), sodium hydroxide (2 g.), and water (150 c.c.) were refluxed for 130 hr. The mixture was steam-distilled, and the distillate was extracted with chloroform. Evaporation of the chloroform, and crystallisation of the residue from ether, gave phenazine in yellow needles (0·29 g., 34%), m. p. 172—173°, identical (mixed m. p. and infrared spectra) with an authentic sample.

The authors thank the Government of Iraq (Ministry of Oil) for a scholarship (to A. S. W.)

THE QUEEN'S UNIVERSITY OF BELFAST. [*Received, October 8th*, 1962.]