CYCLIZATION REACTIONS OF 2,2′-DISUBSTITUTED BIPHENYLS

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Received October 27, 1967

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I. INTRODUCTION

2,2′-Disubstituted biphenyls undergo intramolecular cyclization reactions with particular facility because of the close spatial proximity of the interacting substituents. Although most of the cyclizations observed in the biphenyl series have analogies in intermolecular reactions, some appear to be unique in this system; in many cases, there are obvious possible extrapolations to intermolecular reactions which are yet to be investigated. No systematic study of such cyclization reactions of 2,2′-disubstituted biphenyls appears to have been made, and no review of the many examples of such reactions has appeared, although the dissymmetry of 2,2′-disubstituted biphenyls, cyclized and noncyclized, has been discussed (2, 120).

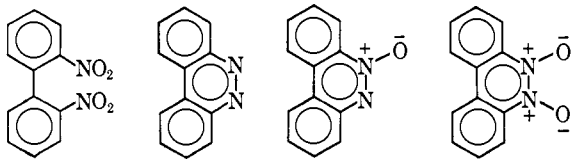
The scope of this review includes cyclizations between 2,2′-situated substituents as well as cyclizations between one *ortho* substituent and the opposite ring of the biphenyl system. Certain aspects of this latter area have been omitted because of extensive coverage elsewhere in other contexts (*e.g.*, the Morgan–Walls and Pictet–Hubert syntheses of phenanthridines). We have attempted to cover the literature through 1966. Some 1967 references are included.

Whenever appropriate, mechanisms, either previously published or originating with the reviewers, are discussed, and the reactions related to known intermolecular analogies. The discussion is organized on the basis of reaction conditions rather than by classes of reactants or products or by mechanism. Diazotizations of biphenylamines are included in the section dealing with acidic reaction conditions. The section dealing with basic reaction conditions also includes interaction with strong nucleophiles. The miscellaneous section deals with cyclizations which involve the intermolecular participation of another reactant. A recurrent theme is the remarkable facilitation of interaction between substituents because of spatial proximity.

II. CYCLIZATIONS BETWEEN *ortho*-SITUATED BIPHENYL SUBSTITUENTS

A. BY REDUCTION

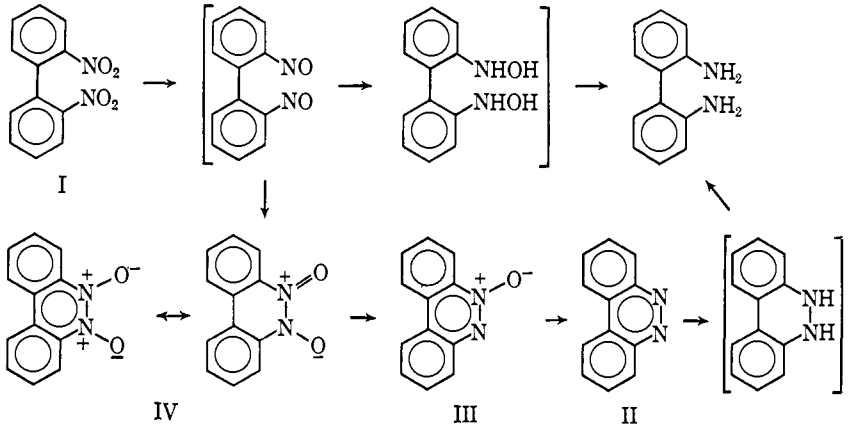
Cyclization concomitant with reduction of 2,2′-disubstituted biphenyls is very common and, in cases involving nitro groups, is almost impossible to avoid. Indeed, the most widely used method of preparing benzo[*c*]cinnolines is reduction of 2,2′-dinitrobiphenyls. The conversion of 2,2′-dinitrobiphenyl (I) to benzo[*c*]-cinnoline (II) can be accomplished by zinc (140), lithium aluminum hydride (13, 51, 64) (and fused ring systems: ref 36, 51, 54), reduced iron (158), ferrous oxalate (18), triethyl phosphite (44), and iron carbonyl (98), and electrolytically (37, 176, 187). Catalytic



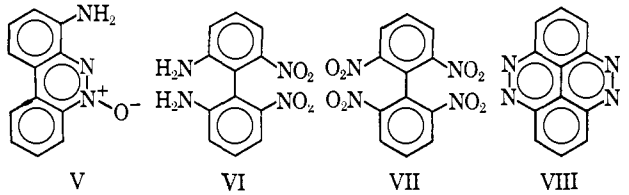
I II III IV

hydrogenation with Raney nickel (65, 166) and palladium on carbon (63, 166) is reported to give II, but reduction to 2,2′-diaminobiphenyl also has been reported (40, 65, 147, 173). The latter is also formed in reductions of I with tin (106, 134) or stannous chloride (65) in hydrochloric acid. Reduction of I with sodium amalgam also gives II (97, 169), but benzo[*c*]-cinnoline N-oxide (III) has been isolated as an intermediate (97, 169). However, when sodium amalgam

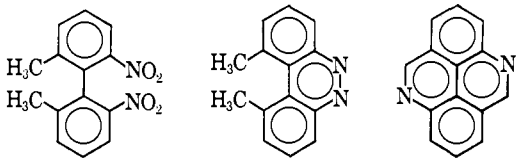
SCHEME I



reduction is applied to analogous condensed ring systems, such as dinitrobinaphthyls, reduction to the diamine is observed (36, 51). The corresponding cinnolines are probable intermediates for they too are reductively cleaved to the diamines by sodium amalgam (36, 51). Reduction of I to III can be accomplished by zinc and acetic acid (64, 176), hydrogenation with palladium (104) or rhodium and base (138), and sodium sulfide (37, 63, 64, 97, 147, 176) (and substituted systems: ref 6, 36, 139), but the latter reagent reduces 4,-4′-bis(trifluoromethyl)-2,2′-dinitrobiphenyl to the corresponding benzo[*c*]cinnoline (148). The stepwise formation of benzo[*c*]cinnoline dioxide (IV) (the intramolecular dimer of 2,2′-dinitrosobiphenyl) and III in the reduction of I with sodium sulfide has been reported (147, 148). Milder sodium sulfide reduction of substituted 2,2′-dinitrobiphenyls gives 2′-nitro-2-biphenylamines (153); the parent compound is best prepared by sodium hydrogen sulfide reduction of I (12, *inter alia*). It was also noted that reduction of 2-amino-2′,3-dinitrobiphenyl yielded 4-aminobenzo[*c*]cinnoline 6-oxide (V) (23). Reduction of III or IV with platinum oxide gives II (147). Zinc and base reduced I to a mixture of III and IV (169), but excess zinc will reduce I all the way to II (169) (also observed in the reduction of substituted benzo[*c*]cinnolines (37)). The tetrasubstituted biphenyls VI and VII are not reduced to cinnoline systems by lithium aluminum hydride (37) or sodium sulfide (37, 176), and VII does not undergo the reaction with sodium amalgam (37) or zinc and acetic



acid (169), but hydrogenation with Raney nickel in basic solution reduces VII to tetraazapyrene (VIII) (166). Also, hydrogenation with Raney nickel in neutral solution reduces VII and VIII to 2,2′,6,6′-tetraaminobiphenyl (166). Presumably the reason for the existing failures is steric hindrance (37), but reduction of 6,6′-dimethyl-2,2′-dinitrobiphenyl (IX) with sodium amalgam proceeds "easily" to 1,10-dimethylbenzo[*c*]cinnoline (X) (95). Electrolytic reduction of IX (in the presence of sodium acetate) gives X in 62%



yield (184). (For preparative aspects of benzo[*c*]cinnolines, see ref 157.)

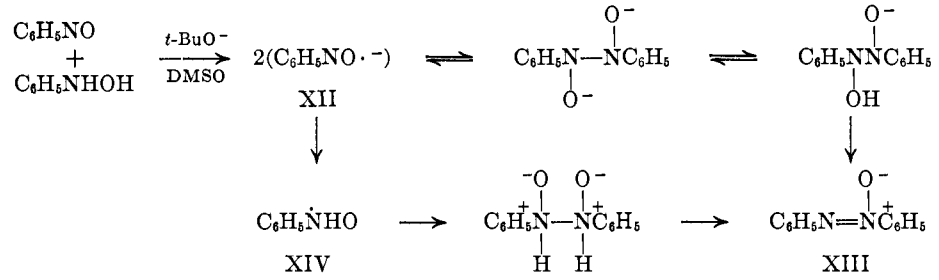
It is interesting that reduction of 6,6′-dimethyl-2,2′-dinitrobiphenyl (IX) with triethyl phosphite affords only 1,10-dimethylbenzo[*c*]cinnoline (X) and no 4,9-diazapyrene (XI) (the oxidized nitrene insertion product) (49).

Reduction of I with phosphine gives the dioxide IV in 75% yield (27), but reduction of a substituted system gives the corresponding monoxide (26). When 2-nitronaphthalene or 6-nitroisoquinoline is reduced under the same conditions, the corresponding azoxy compound and its cyclization product, *i.e.*, a fused ring benzo[*c*]cinnoline, is formed (27).

The Raney nickel–hydrazine reducing system (71, 137) afforded insight on the mechanism of the reductions described above. Moore and Furst (124) were interested in obtaining a good preparation of 2,2′-diaminobiphenyl by reduction of I, for it had been found that, if the reduction was carried out catalytically with palladium on charcoal or Raney nickel, the results were erratic (24, 124). It was found that the reduction of I with Raney nickel and hydrazine sequentially produced IV, III, II, and 2,2′-diaminobiphenyl depending on the conditions employed, the bracketed compounds (Scheme I) being probable intermediates (70, 124).

A similar stepwise reduction can be observed in the polarographic reduction of I (147). Benzo[*c*]cinno-

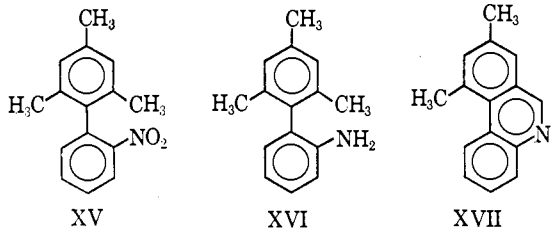
SCHEME II



line was isolated in 82% yield in the reduction of 2,2′-dinitrobiphenyl with hydrazine and 5% ruthenium on carbon in 5% ethanolic base (138).

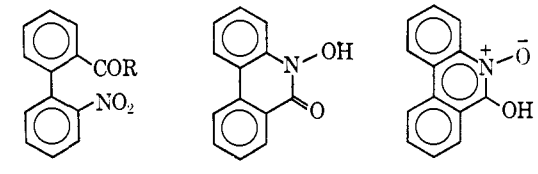
An alternative mechanism that may apply to the above reductions is based on the observation (150) that under basic conditions nitrosobenzene and phenylhydroxylamine react to give the radical anion XII which couples and loses water to give azoxybenzene (XIII). In nonbasic media, phenyl nitroxide (XIV), the protonated form of XII, is formed, which eventually yields azoxybenzene (150) (Scheme II).

Pyrolysis of 2′-nitro-2,4,6-trimethylbiphenyl (XV) with ferrous oxalate at 300° produced the amine XVI in 27% yield and the phenanthridine XVII in 23% yield (1). Smolinsky and Feuer were able to cyclize XV to XVII by heating at 350° (no ferrous oxalate). They also cited evidence obtained from the reactions of *ortho*-substituted nitrobenzenes which indicates that triethyl phosphite reductions involve nitrenes but that ferrous oxalate reductions do not (164).



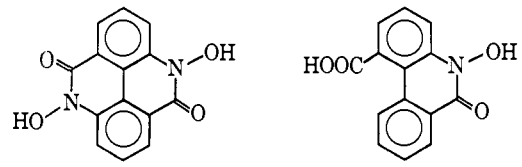
XV XVI XVII

Cyclization also occurs upon reduction of biphenyls containing *ortho,ortho′*-situated nitro and carboxylic acid groupings. Reduction of 2-nitrobiphenyl-2′-carboxylic acid (XVIII) with zinc and hydrochloric acid gives mostly phenanthridone and some N-hydroxyphenanthridone (XXI) (76), while catalytic reduction in alkaline solution gives phenanthridone (128a). Surprisingly, XXI is formed simply upon heating XVIII in tetralin; it was suggested that reduction of the nitro group was accomplished by the solvent in a noncatalyzed, homogeneous hydrogen-transfer reaction followed by cyclodehydration of the resulting hydroxylamino derivative (76). Compound XXI is also formed upon catalytic reduction (best in the presence of acid) of the ester (XIX) and amide (XX) (57, 128a). By comparison with models, XXI was shown to be the correct structure for the XXI–XXII tautomeric pair (57, 128a), in agreement with results on other cyclic hydroxamic acids. Reduction of 2,2′-dinitrobiphenyl-6,6′-dicarboxylic acid with zinc and ammonium chloride (72) or catalytic reduction of the coresponding dimethyl ester in the presence of acid (128a) gives 4,9-dihydroxy-5,10-dioxo-4,9-diazapyrene (XXIII). Some of these results led to the conclusion (76) that N-hydroxyphenanthridone-1-carboxylic acid (XXIV) was obtained by Bell (25) in the reduction of 2-nitrobiphenyl-2′,6-dicarboxylic acid with zinc and hydrochloric acid; it was originally claimed (25) that phenanthridone-1-carboxylic acid had been the product. The elemental analysis is in agreement with the revised structural assignment.



XVIII, R = OH
XIX, R = OCH_3
XX, R = NH_2

XXI XXII

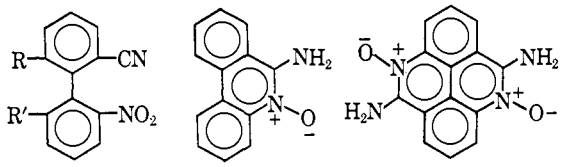


XXIII XXIV

Intramolecular trapping of the hydroxylamine formed upon catalytic reduction of a 2-nitro group can also be effected by a 2′-situated nitrile grouping. Thus, catalytic reduction of 2-cyano-2′-nitrobiphenyl (XXV) gives 6-aminophenanthridine 5-oxide (XXVII); analogous reduction of 2,2′-dinitro-6,6′-dicyanobiphenyl (XXVI) gives 5,10-diamino-4,9-diazapyrene 4,9-dioxide (XXVIII) (57, 128a).

Catalytic hydrogenation of methyl 2-nitro-2′-biphenylylacetate with platinum leads to the seven-membered lactam XXIX (128).

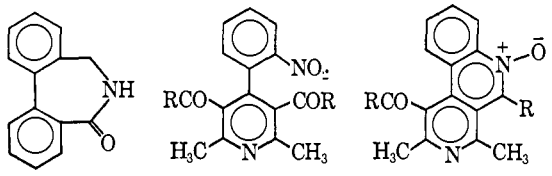
Reductive cyclizations have also been observed with a series of 4-(2-nitrophenyl)pyridine-3-carboxylic acid



XXV, R = R′ = H
XXVI, R = NO_2, R′ = CN

XXVII

XXVIII



XXIX

XXX, R = OC_2H_5
XXXI, R = CH_3

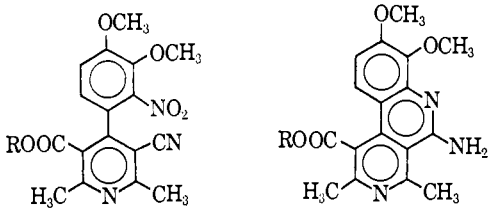
XXXII, R = OC_2H_5
XXXIII, R = CH_3

derivatives; XXX and XXXI yield the azaphenanthroline oxides XXXII and XXXIII (74).

If the reducing medium is changed to iron in aqueous acid or to sodium hydrosulfite, the product from XXXIV is XXXV (55, 136). There is no evidence presented to distinguish between cyclization of the derived amine or, alternately, reduction of an intermediate N-oxide.

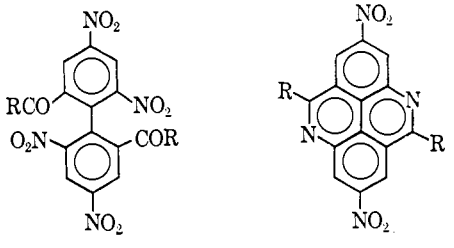
A zinc chloride induced cyclization between *ortho*-situated biphenylyl nitro groups and methyl groups (to give a fused quinoline system) has been noted (99).

Internal Schiff base formation has also been observed in the reduction of XXXVI to XXXVII (67).



XXXIV, R = C_2H_5

XXXV, R = C_2H_5

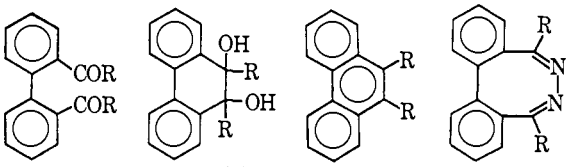


XXXVI

XXXVII

R = C_6H_4R';
R′ = H, *p*-CH_3, *p*-Cl, *p*-OCH_3

The reduction of 2,2′-dicarbonylbiphenyls often proceeds with cyclization. Reduction of 2,2′-diformylbiphenyl (XXXVIII, R = H) with sodium amalgam gives *cis*-9,10-phenanthrenediol (XXXIX, R = H). Likewise reduction of a series of 2,2′-diaroylbiphenyls (XXXVIII, R = aryl) with sodium amalgam, zinc, and base, or magnesium–magnesium iodide, gives varying yields of *cis*-9,10-diaryl-9,10-phenanthrenediols (XXIX, R = aryl) (126).



XXXVIII

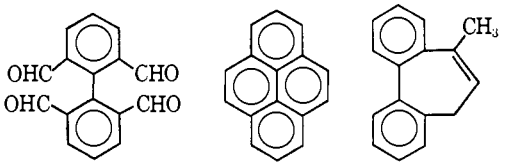
XXXIX

(*cis*)

XL

XLI

Treatment of 2,2′-diformylbiphenyl with hydrazine under a variety of conditions gives phenanthrene (XL, R = H), obtained in quantitative yield in hot acetic acid (9, 10). A similar reaction occurs with 2,2′-diformyl-5,5′-dinitrobiphenyl, but 2,2′-diformyl-6,6′-dimethylbiphenyl gives only 2,2′,6,6′-tetramethylbiphenyl (45% yield) and no 4,5-dimethylphenanthrene (9, 10). Curiously, 2,2′,6,6′-tetraformylbiphenyl (XLII) cyclizes readily under the same conditions to give pyrene (XLIII) (9, 10). The ketones XXXVIII (R = CH_3, C_2H_5, C_6H_5) give, under the same conditions, the dibenzodiazocines XLI along with some of the corresponding phenanthrenes XL (9, 11). The diazocines

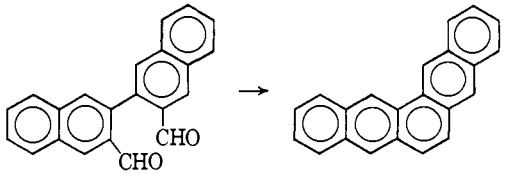


XLII

XLIII

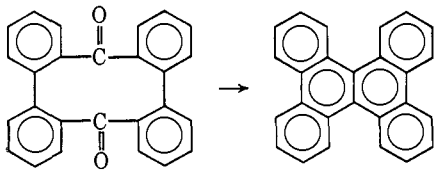
XLIV

are relatively heat stable and are therefore not precursors of the phenanthrenes (9, 11, 73). However, when the diazocine XLI (R = CH_3) is subjected to Wolff–Kishner conditions, 9,10-dimethylphenanthrene is formed (73). On the other hand, 2,2′-diacetylbiphenyl under the same conditions gives XLIV, derived from the intramolecular aldol condensation product (73). Clemmensen reduction (zinc amalgam in hydrochloric acid) of 2,2′-diacetylbiphenyl gives 9,10-dimethylphenanthrene in quantitative yield (73). More complicated diformylbiphenyls, such as 3,3′-diformyl-2,2′-binaphthyl (XLV) (8), XLVI (167), and the aldehyde acid XLVII (179) have been reduced to aromatic systems with hydrazine.

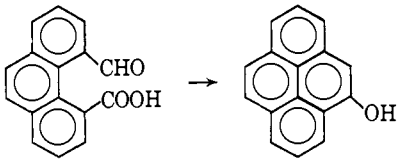


XLV

Recently, it was shown that 2,2′-diformylbiphenyl gives 9,10-epoxyphenanthrene (XLVIII) in 89% yield upon treatment with tris(dimethylamino)phosphine (132). The epoxy compound rearranges to 9-hydroxy-

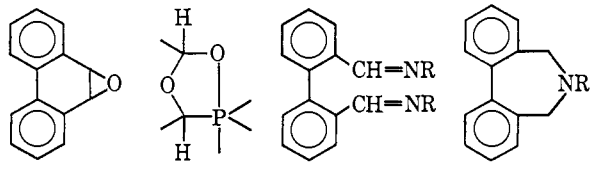


XLVI



XLVII

phenanthrene in acid or when heated. The reaction was also performed on fused-ring diformylbiphenyls (35, 132). Cyclization is probably occurring *via* the intermediate XLIX (*cf.* ref 106a).

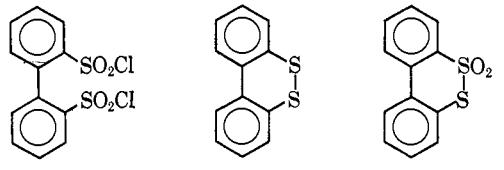


XLVIII XLIX L LI

R = $CH_2C_6H_5$, CH_3, C_6H_5

Reduction of a series of Schiff bases (L) derived from 2,2′-diformylbiphenyl gives dihydrodibenzo[*c,e*]azepines (LI). The same product is obtained when L (R = C_6H_5) is reduced catalytically with Raney nickel (75).

Zinc and hydrochloric acid reduction of the disulfonyl chloride LII gives the dithiane LIII in 50–60% yield. The dithiane dioxide LIV is obtained from LII by treatment with bisulfite followed by acid. The reaction proceeds *via* the disulfonic acid which spontaneously rearranges (20). The dithiane LIII is also obtained by reduction of LII with hydriodic acid in acetic acid (7).

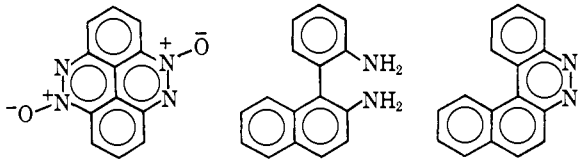


LII LIII LIV

B. BY OXIDATION

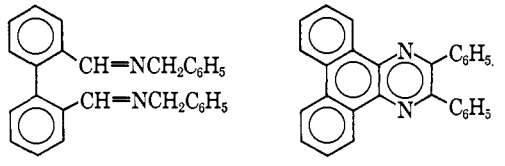
Although there are fewer examples of oxidative than of reductive cyclizations in the biphenyl series, it is again evident that cyclization is facilitated by special proximity of the reacting groups.

Benzo[*c*]cinnolines can be prepared by oxidation of the corresponding diaminobiaryls, but the yields are not as good as in the reduction of the dinitro compounds (52). Moreover, the diamino compounds are most often prepared from dinitro compounds. Thus, oxidation of 2,2′-diaminobiphenyl with sodium perborate yields benzo[*c*]cinnoline (50%; 35% over-all from 2,2′-dinitrobiphenyl) (52). Oxidation with hydrogen peroxide in acetic acid gives similar yields of the cinnoline N-oxide. Oxidations of other diaminobiaryls were performed, and yields were lower than those cited above (52). Oxidation of 1,10-diaminobenzo[*c*]cinnoline with peracetic acid produces 4,5,9,10-tetraazapyrene 4,9-dioxide (LV) (or the 4,10-dioxide) (80) in 70% yield. However, oxidation of 1-(2-aminophenyl)-2-naphthylamine (LVI) with persulfuric acid gives dibenzo[*c,f*]cinnoline (LVII) in 17% yield (14).



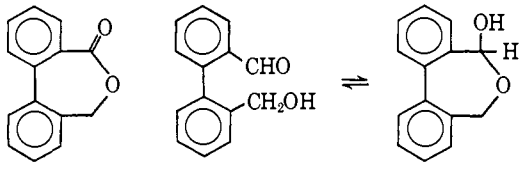
LV LVI LVII

Dehydrogenation of the imine LVIII (from benzylamine and 2,2′-diformylbiphenyl) with copper chromite in refluxing dimethylformamide leads to 2,3-diphenyldibenzo[*f,h*]quinoxaline (LIX) in 14% yield (75).



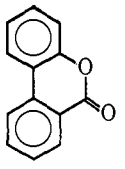
LVIII LIX

Oxidation of 2,2′-bis(hydroxymethyl)biphenyl with nitrogen tetroxide gives a mixture of 2,2′-diformylbiphenyl (15%) and the lactone LX (20–65%); the latter is probably formed *via* the aldehyde carbinol LXI and the hemiacetal LXII (8).

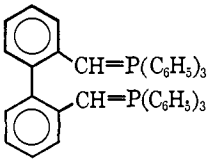


LX LXI LXII

Merely warming 2′-methoxy-2-biphenylcarboxylic acid with thionyl chloride in an attempt to form the acid chloride produces 3,4-benzocoumarin (LXIII) in quantitative yield and methyl chloride. This demethylation, which is much more facile than usual, was attributed to the proximity of the reacting groups (149).



LXIII



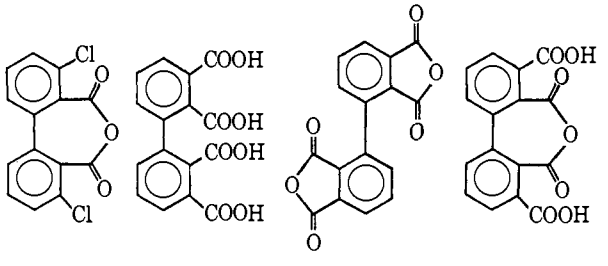
LXIV

Chromic acid oxidation of 2,2′-divinylbiphenyl yields phenanthrenequinone (no yield given) (73). The autoxidation product of the bisphosphorane LXIV is phenanthrene in 45% yield (32). Ferric chloride oxidizes 2,2′-dimercaptobiphenyl to the dithiane LIII (7).

C. BY ACTION OF ACID

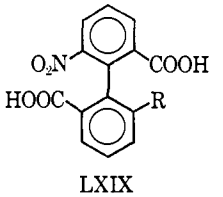
This section includes diazotizations of 2,2′-diaminobiphenyls and subsequent reactions, although the latter involve various processes including reduction. These reactions result in particularly facile cyclizations.

Intramolecular anhydride formation between the 2 and 2′ positions can occur in the biphenyl series; for example, 3,3′-dichloro-2,2′-diphenic anhydride (LXV) is formed in quantitative yield when the corresponding diphenic acid is heated with acetic anhydride (85).

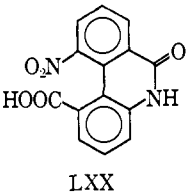


LXV LXVI LXVII LXVIII

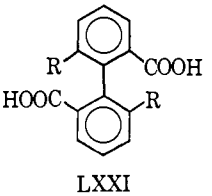
However, reaction of the tetraacid LXVI with acetyl chloride yields only the dianhydride LXVII and none of the diphenic anhydride LXVIII (94). Hydrolysis of 2-acetamido-2′-biphenylcarboxylic acids yields lactams as products; for example, LXX is formed from LXIX (153) and the bislactam LXXII from LXXI (95).



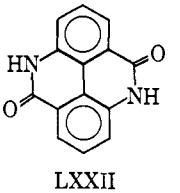
LXIX
R = NHCOCH$_3$



LXX



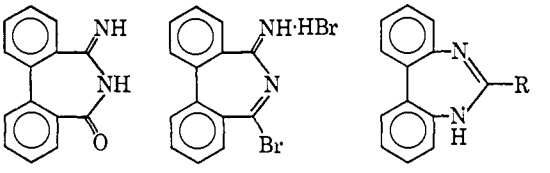
LXXI
R = NHCOCH$_3$



LXXII

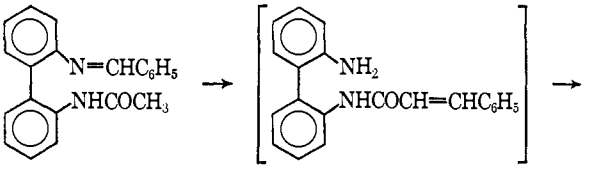
Cyclization of 2,2′-dicyanobiphenyl occurs both with hydrobromic acid in acetic acid to give LXXIII, and with hydrobromic acid in benzene to give LXXIV (90). Monobenzoyl 2,2′-diaminobiphenyl is cyclized with phosphorus trichloride to the diazepine LXXV (R = C_6H_5) (151).

A small amount of the 6-methyldiazepine LXXV (R = CH_3) is obtained by diazotization of monoacetyl-2,2′-diaminobiphenyl, the major product being

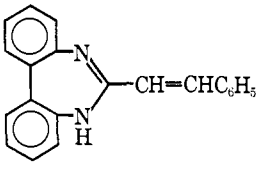


LXXIII LXXIV LXXV

N-acetylcarbazole (151). An interesting cyclization occurs when 2′-acetamido-2-biphenylamine benzylidenimine (LXXVI) is heated with phosphorus oxychloride and benzene. A styryldiazepine LXXVIII is formed, probably *via* the intermediacy of LXXVII, for the latter could be independently prepared (from 2,2′-diaminobiphenyl and cinnamic anhydride) and cyclized by phosphorus oxychloride to give the same product, LXXVIII (33).



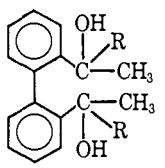
LXXVI LXXVII



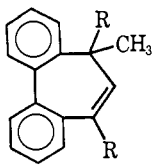
LXXVIII

Intramolecular carbonium ion capture under acidic reaction conditions is observed. Both LXXIX and LXXX can be cyclized to the respective dibenzotropylidenes LXXXII and LXXXIII, the former with acetic acid (185) and the latter wth 2-naphthalenesulfonic acid at 140° (61). The latter product (LXXXIII) is also obtained from 2,2′-bis(2-propenyl)-biphenyl with either hydrobromic or sulfuric acid (61). A dihydrooxepin (LXXXIV, R = H) is obtained from the corresponding bis secondary carbinol LXXXI with 20% sulfuric acid. Likewise, the analogous bis-*t*-carbinol LXXX with sulfuric acid yields the corresponding oxepin LXXXIV (R = CH_3) which in turn produces LXXXIII with hydrobromic acid (61).

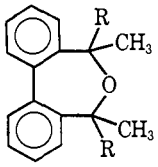
Primary carbinols are also cyclized in acid. Conversion of 2,2′-bis(hydroxymethyl)-6,6′-dimethylbi-



LXXIX, R = C_6H_5
LXXX, R = CH_3
LXXXI, R = H

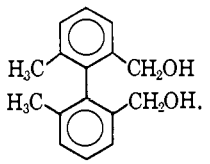


LXXXII
LXXXIII

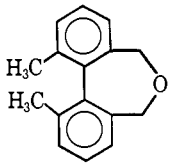


LXXXIV
R = H, CH_3

phenyl (LXXXV) to the oxepin LXXXVI has been accomplished with *p*-toluenesulfonic acid, both on racemic (186) and optically active starting material (122), the latter yielding optically active product. Analogous cyclizations have been carried out in several cases with *p*-toluenesulfonyl chloride (121, 122, 135a).

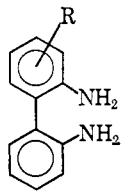


LXXXV



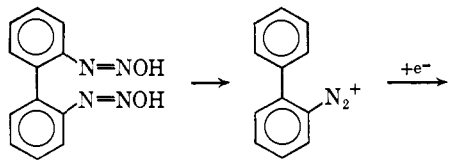
LXXXVI

Diazotization of a series of substituted 2,2′-diaminobiphenyls (LXXXVII) followed by reduction with hypophosphorous acid gives the corresponding benzo[*c*]cinnolines in poor to fair yields (22). Diazotization in the presence of cuprous bromide gave a mixture of benzo[*c*]cinnoline, carbazole, and 2,2′-dibromobiphenyl (58), although only the latter was reported in a later investigation (79). Benzo[*c*]cinnoline is also the product when the diazotization is carried out with sodium arsenite (154).

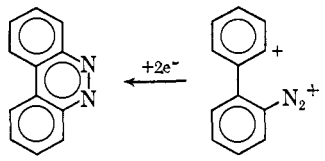


LXXXVII, R = 3-NO_2, 4-NO_2, 5-NO_2, 5-Br

The mechanism of these reactions has been discussed. Saunders and Waters favor cyclization *via* a radical cation LXXXVIII or a dication LXXXIX (155).



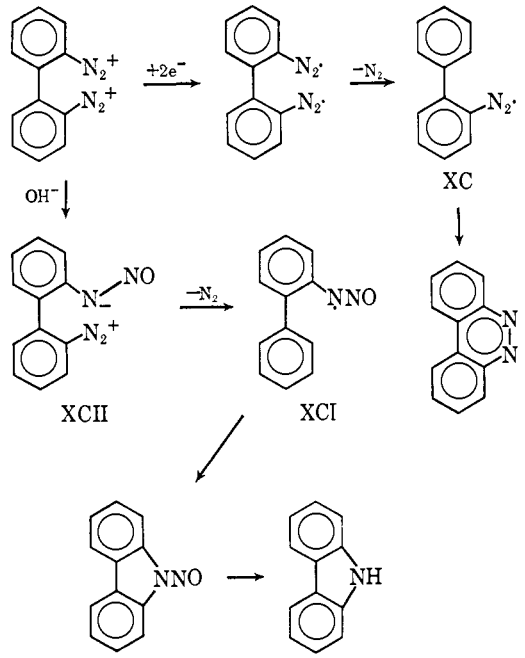
LXXXVIII



LXXXIX

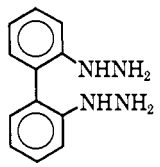
On the other hand, Hodgson favors coupling of the diradical XC or cyclization of the diradical XCI derived from the diazotate XCII, eventually giving carbazole (78). Both authors cite analogies from diazonium reactions on more simple species.

When 2,2′-dihydrazinobiphenyl (XCIII) (prepared by stannous chloride reduction of diazotized 2,2′-diaminobiphenyl) is heated with hydrochloric acid at 150°, benzo[*c*]cinnoline is produced (no yield given) (79, 171). Sodium nitrite-^{15}N has been used in the diazotization; the resulting dihydrazine XCIII (labeled



XCII XCI XC

in both β-nitrogens) yields benzo[*c*]cinnoline that is only partially labeled, indicating more N–N than C–N bond cleavage (79). Contrary to previous reports (89, 102, 103), later information has indicated that no scrambling of nitrogen atoms occurs in diazotization reactions, at least at 50° (34). Although the evidence for scrambling has been reaffirmed (103a), the conclusions concerning N–N bond cleavage described above appear to be well founded, for the amount of scrambling observed is less than the isotopic loss observed for XCIII (79, 103a).



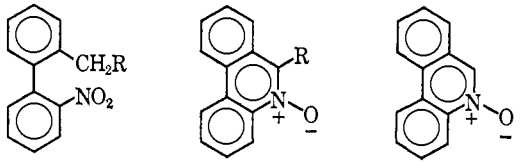
XCIII

D. BY ACTION OF BASE

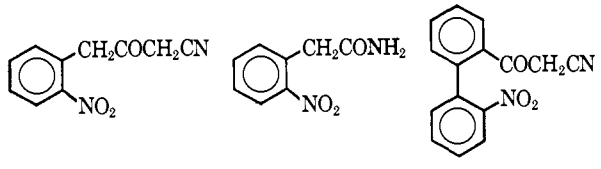
This section is concerned with 2,2′-disubstituted biphenyl cyclizations performed under basic conditions as well as cyclizations initiated by nucleophiles.

Attempts to hydrolyze the ester XCIV (R = $COOCH_3$) led instead to cyclization, the oxide XCV (R = $COOCH_3$) or phenanthridine 5-oxide (XCVI) being isolated. The reaction was extended to other active methylene compounds (see Table I). Cyclization occurs with compound XCIV when R = $COOCH_3$, CN, COC_6H_5, $CONH_2$ (129), and $SO_2C_6H_5$ (127), and fails when R = COOH, H, OH, Br (129), and C_6H_5 (127). Compound XCIV (R = NO_2) was not rigorously identified as such and also failed to cyclize (129). The yields of the products XCV and XCVI appear to depend on the exact conditions; total cyclization yields range from 65% for the ester to 87% for the nitrile. In regard to the product distribution, presumably in the reactions with the ester and the amide, hydrolysis to the acid takes place and subsequent decarboxylation gives phenanthridine 5-oxide (XCVI). Ketone cleavage of XCV (R = COC_6H_5) probably occurs under the basic conditions to yield XCVI (129). Displacement of the sulfonyl group by hydroxyl was postulated to occur with XCV (R = $SO_2C_6H_5$) yielding the observed products (127). This nucleophilic aromatic substitution is undoubtedly facilitated by the adjacent N-oxide grouping. The mechanism of these condensations is most likely attack of the benzyl carbanion, formed from the active methylene group, on the nitro group with subsequent loss of water to give the oxide XCV (127, 129). The mechanism of carbanionic attack on nitro groups has been discussed in more detail in connection with cyclizations of *o*-nitrobenzyl compounds (105). The biphenyl cyclizations represent some of the few examples where such a mechanism can be easily demonstrated (105). The above reaction fails with compounds XCVII–XCIX (127).

TABLE I



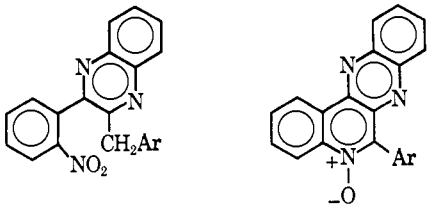
XCIV	XCV	XCVI
R = $COOCH_3$	+ (and R = COOH)	+
R = CN	+	None
R = COC_6H_5	None	+
R = $CONH_2$	+	+
R = $SO_2C_6H_5$	(R = OH, + $C_6H_5SO_2H$)	



XCVII XCVIII XCIX

The kinetics of the cyclization of XCIV have been studied and it was found that the formation of XCV and XCVI from XCIV (R = $COOCH_3$) had the same second-order rate constant, indicating a rapid cyclization and a subsequent rate-determining saponification (130).

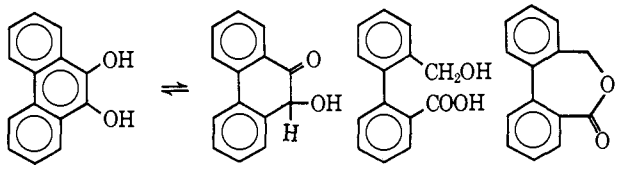
In contrast to the failure of 2-benzyl-2′-nitrobiphenyl to cyclize in base (127), the quinoxaline C cyclizes to CI by rather mild treatment with base (21). In the latter case, the methylene hydrogens are more acidic than in the former, allowing formation of the requisite carbanion.



C CI

In basic solution, 2-amino-2′-nitrobiphenyl cyclizes to benzo[*c*]cinnoline 5-oxide (127). The corresponding 5-bromo compound has also been cyclized (53). Benzyltrimethylammonium hydroxide rather than sodium hydroxide or alkoxide employed earlier (53, 127) has been used in the cyclization of other substituted aminonitrobiphenyls (23, 139).

Conflicting results have been reported concerning the intramolecular benzoin condensation of 2,2′-diformylbiphenyl. Kenner and Turner reported the cyanide-catalyzed product to be an "ill-defined" sample of phenanthrene-9,10-diol (CII) which was not oxidized to phenanthrenequinone (96). Weitzenböck, on the other hand, reported the preparation of phenanthrenequinone in 50% over-all yield *via* chromic acid oxidation of the intermediate diol (CII) (182). Furthermore, Mayer reported the direct formation of phenanthrenequinone in the above benzoin condensation and obtained similar results for 2,2′-diformyl-6,6′-dimethylbiphenyl and 2,2′-diformyl-6,6′-dimethoxybiphenyl (115). As far as is known, the situation has not been clarified.



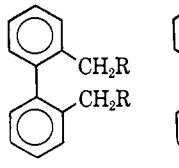
CII CIII CIV

An intramolecular Cannizzaro reaction has been observed by the action of concentrated aqueous potassium hydroxide on 2,2′-diformylbiphenyl affording 2-hydroxymethyl-2′-biphenylcarboxylic acid (CIII) and the lactone CIV (96).

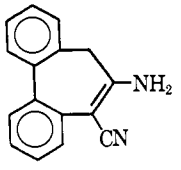
Thorpe and Dieckmann cyclizations have been carried out on 2,2′-disubstituted biphenyls. Cyclization of the

dinitrile CV (R = CN) with sodium ethoxide affords the aminonitrile CVI in 80% yield (96) (for cyclization in a substituted system, *cf.* ref 135b). Thorpe cyclizations have also been accomplished with several tetrasubstituted biphenyls including a double cyclization of a tetracyano compound (121, 122, 123b). Treatment of the diester CV (R = $COOCH_3$) with sodium in toluene gives the keto ester CVII in 84% yield (94). Sodium in benzene cyclizes the sulfone ester CVIII to the keto sulfone CIX in 76% yield (61). Treatment of dimethyl 6,6′-dimethyldiphenate (CX) with sodium and xylene produces 4,5-dimethylphenanthrenequinone in 36% yield (186). An acyloin cyclization yielding a ten-membered ring has been accomplished in the 2,2′-disubstituted biphenyl series (123a).

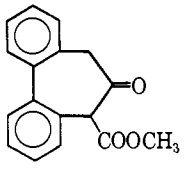
A reaction that appears to be a Hofmann rearrangement followed by cyclization has also been observed. Treatment of the diamide (CXI) of diphenic acid with



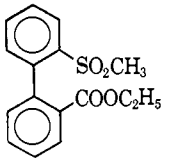
CV



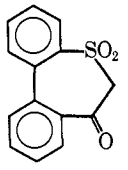
CVI



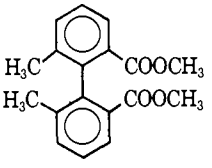
CVII



CVIII

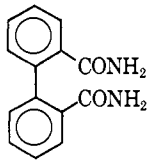


CIX

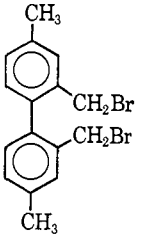


CX

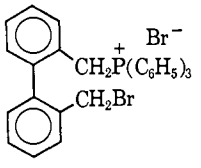
bromine in potassium hydroxide affords phenanthridone in 94% yield (135). Either one amide group undergoes rearrangement to the amine which then cyclizes to give the product, or cyclization analogous to uracil formation (from maleic acid diamide) (37a) occurs, with subsequent hydrolysis and ring closure to phenanthridone.



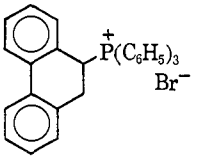
CXI



CXII



CXIII



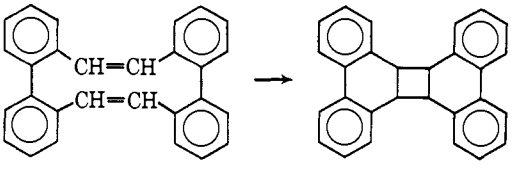
CXIV

Treatment of 2,2′-bis(bromomethyl)-4,4′-dimethylbiphenyl (CXII) with phenyllithium affords 2,7-dimethyl-9,10-dihydrophenanthrene (133). 2,2′-Bis(bromomethyl)-6,6′-dimethylbiphenyl analogously yields 4,5-dimethyl-9,10-dihydrophenanthrene (29a), and other similar cyclizations are known (see 29a for references). The reaction probably proceeds by metalation and subsequent intramolecular cyclization. Retention of optical activity has been observed (123). Treatment of the phosphonium salt CXIII with alkoxide affords the cyclic phosphonium salt CXIV in 87% yield, the reaction proceeding *via* an intermediate phosphorane (30, 31).

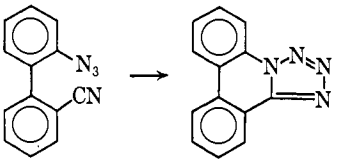
E. BY THERMAL INDUCTION

Cyclizations discussed in this section are those that require no other agent than application of heat.

1,2,3,4,7,8,9,10 - Tetrabenzocyclododecahexaene (CXV) cyclizes upon heating at 180° to the fused-ring cyclobutane CXVI in 64% yield. The latter upon heating to 240° gives phenanthrene in 93% yield (183).



CXV → CXVI



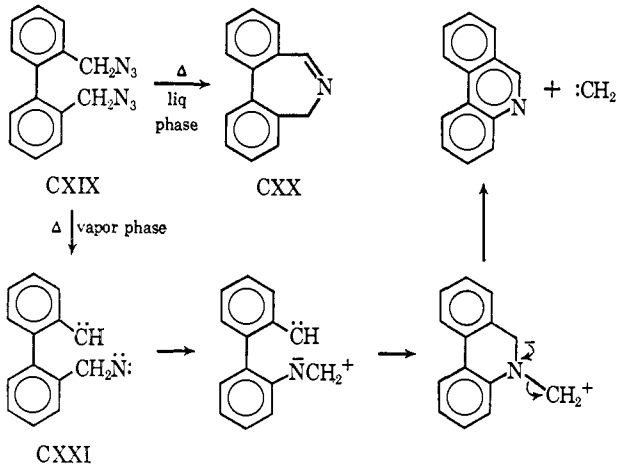
CXVII → CXVIII

An intramolecular 1,3-dipolar addition occurs when 2-azido-2′-cyanobiphenyl (CXVII) is heated at 180°; 9,10-tetrazolophenanthridine (CXVIII) is produced in 72% yield (160).

Although only noncyclized products are observed when 2-azidomethylbiphenyl is heated, 2,2′-diazidomethylbiphenyl (CXIX) gives 3,4,5,6-dibenzoazepine (CXX) when heated in diphenyl ether, the reaction presumably proceeding *via* the corresponding azidocarbene (49). Heating CXIX in the vapor phase gives phenanthridine, perhaps *via* rearrangement of the nitrenecarbene CXXI (Scheme III) (49). The proposed expulsion of carbene in the last step is remarkable and should be verified by experiment.

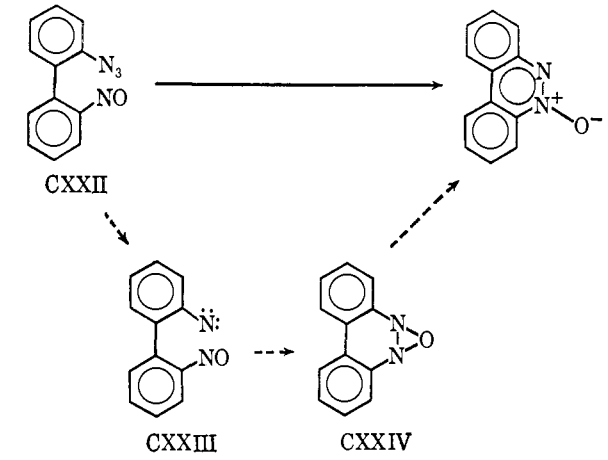
When 2-azido-2′-nitrosobiphenyl (CXXII) is refluxed in toluene or photolyzed, benzo[*c*]cinnoline 5-oxide is produced probably *via* the nitrene CXXIII (131) and subsequently either by formation of the oxadiaziridine CXXIV (131) followed by rearrangement or by direct attack of the nitrene on the nitrogen lone electron pair.

SCHEME III



CXXI

Benzonitrile and 6-phenylphenanthridine (CXXVI, R = H) are produced when the 1,4-diazocine CXXV (R = H) is refluxed in mesitylene (5). The yield of



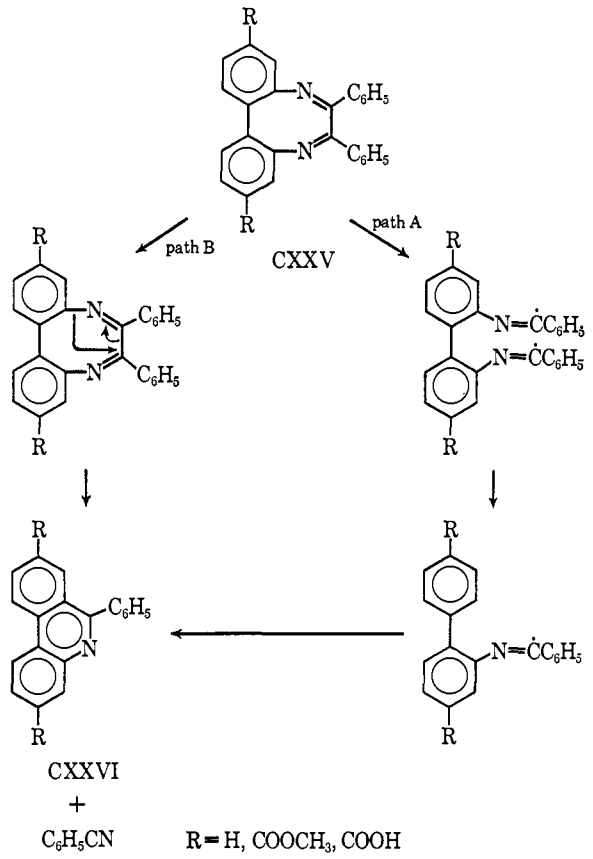
CXXVI (R = $COOCH_3$) from CXXV (R = $COOCH_3$) was comparable (67%; no yield was given for R = COOH). The reaction probably proceeds (Scheme IV) either by fragmentation and recombination (path A) or by a cyclic process (path B) (5).

Pyrolysis of 2,2′-bitolyl (2,2′-dimethylbiphenyl) at red heat affords phenanthrene (no yield stated) (116).

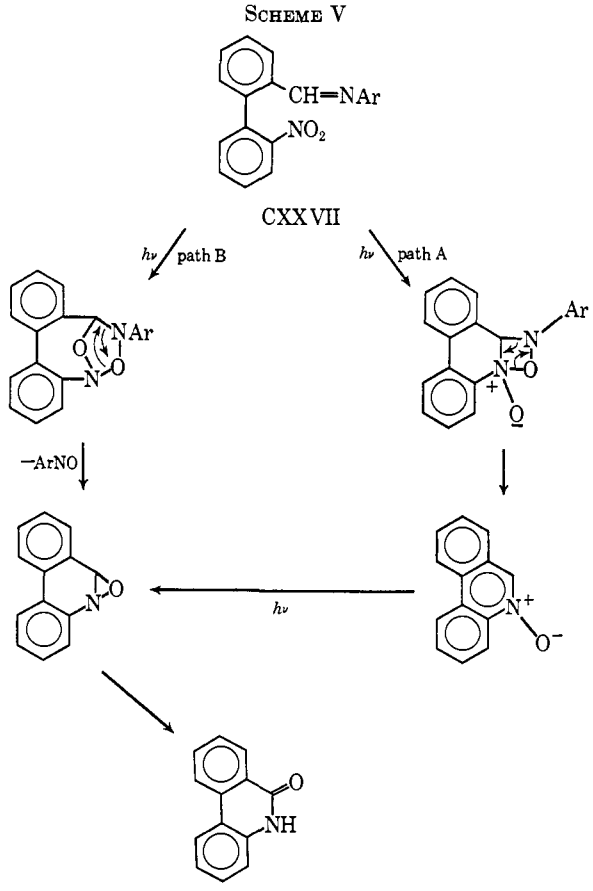
F. BY PHOTOLYSIS

Irradiation of 2-formyl-2′-nitrobiphenyl *p*-chlorophenyl anil (CXXVII) (in ethanol) gives phenanthridone (174). Two possible mechanisms are shown in Scheme V. It was shown independently that phenanthridone is the photolysis product of phenanthridine 5-oxide. The authors favor path B (174) because of precedence for such a reaction in other systems (38, 83, 165). In addition, photolysis of 2-(cyanoanilinomethyl)-2′-nitrobiphenyl (CXXVIII) yields 6-cyanophenanthridine (174). The reaction also proceeds extremely rapidly in base, probably *via* path D (Scheme VI) (174). The latter strongly suggests that the cycloaddition of the

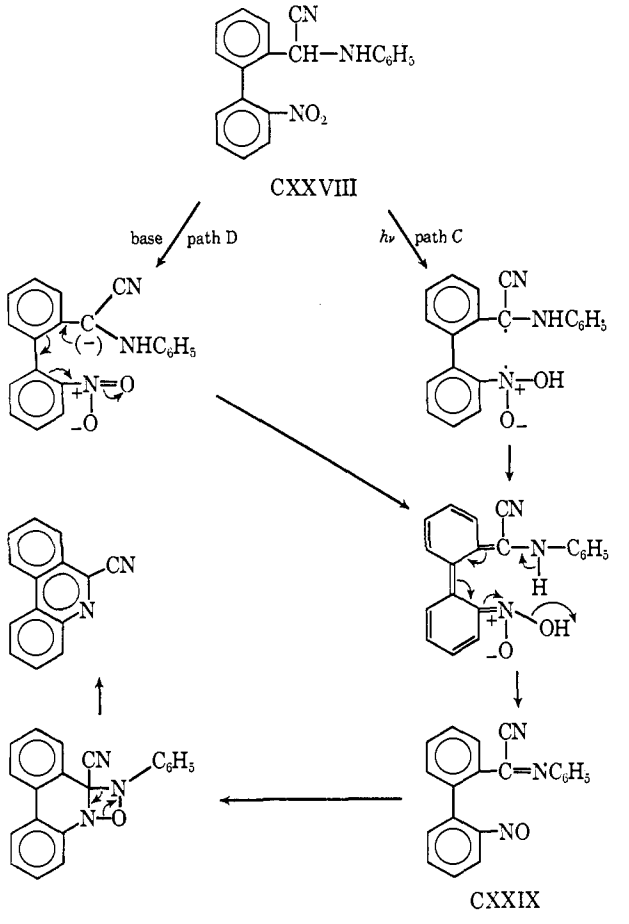
SCHEME IV



SCHEME V



SCHEME VI



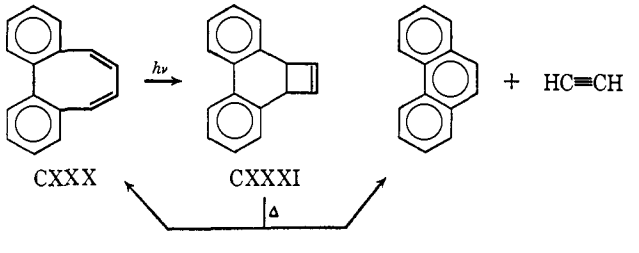
CXXVIII

CXXIX

nitroso intermediate CXXIX may not be photochemical. If so, the cyclization of CXXIX is especially interesting when compared with similar intermolecular reactions (40, 42, 66, 88, 173), and it would be interesting to look for other examples. Photochemical condensation products of nitrosobenzene, *viz.*, azobenzene and azoxybenzene, were detected in the photochemical reaction, and nitrosobenzene was detected in the base-catalyzed reaction (174).

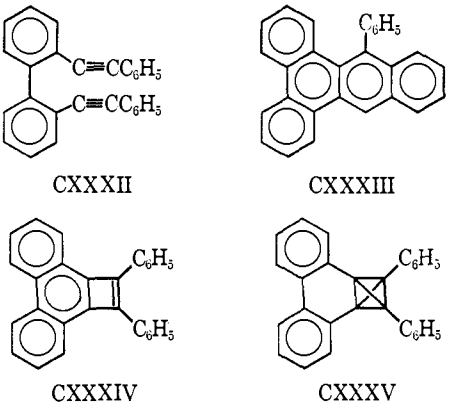
Photolysis of 2,2′-diformylbiphenyl yields phenanthrenequinone (best yield, in acetone, 32%) (75). However, a trace of benzoyl peroxide is required. It was not stated whether or not benzoyl peroxide in the absence of light allows the reaction to occur.

It has been found that photolysis of 1,2,3,4-dibenzocyclooctatetraene (CXXX) gives an almost quantitative yield of the fused-ring cyclobutene CXXXI (178). The reaction can be reversed with heat, but with some loss because of a concomitant fragmentation reaction leading to phenanthrene and acetylene (178).



CXXX CXXXI

Photolysis of 2,2′-bis(phenylethynyl)biphenyl (CXXXII) gives 9-phenyldibenz[*a*,*c*]anthracene (CXXXIII) (182a) and not CXXXIV or CXXXV as previously proposed (91). No intermediates could be detected. Thermolysis of CXXXII also gives CXXXIII (182a).



CXXXII CXXXIII

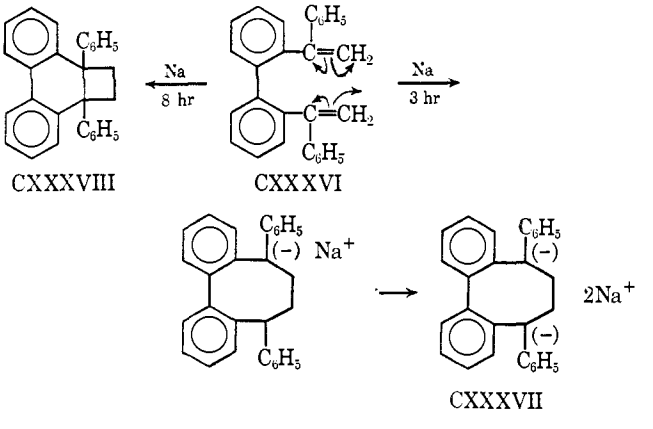
CXXXIV CXXXV

G. BY RADICAL OR METAL INITIATION

Kenner and Turner observed that 2,2′-bis(bromomethyl)biphenyl cyclizes to 9,10-dihydrophenanthrene when treated with sodium (no yield given) (96).

Treatment of 2,2′-bis(1-styryl)biphenyl (CXXXVI) with sodium metal for 3 hr yields the organosodium compound CXXXVII (185). The proposed mechanism is as shown in Scheme VII. If the reaction is carried out for 8 hr, the product is the cyclobutane compound CXXXVIII. It is assumed that CXXXVIII is formed by the disproportionation of CXXXVI and CXXXVII (185).

SCHEME VII



CXXXVIII CXXXVI

CXXXVII

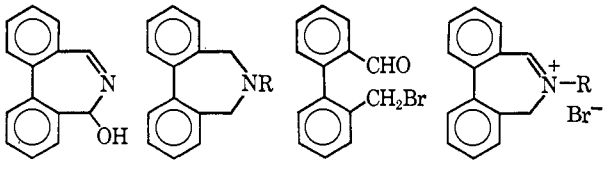
H. BY MISCELLANEOUS AGENTS

The reactions discussed in this section are those in which the two biphenyl substituents become bridged by another group.

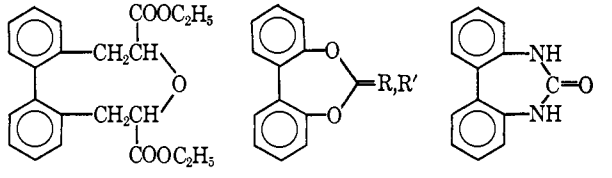
When 2,2′-diformylbiphenyl is refluxed briefly with ammonium hydroxide, the hydroxyazepine CXXXIX is formed in 97% yield (75). Reductive aminations with several amines were also performed, yielding the dihydrodibenzazepines CXXXIXa (75) also formed from 2,2′-bis(bromomethyl)biphenyl and primary amines (141a). Compounds analogous to CXXXIX are probably intermediates. Reaction of 2-bromomethyl-2′-formylbiphenyl (CXL) with aromatic primary amines leads directly to N-aryl-5H-dibenz[*c,e*]-azepinium bromides (CXLa), probably by initial alkylation of the amine followed by intramolecular hemiaminal formation and dehydration (141a). The reaction product of 2,2′-diformylbiphenyl with ethyl bromoacetate and zinc does not give the expected doubly unsaturated Reformatzky product, but rather a compound which contained one molecule of water more, which showed (uv) only biphenyl absorption and which was saturated toward hydrogen. Structure CXLI has been suggested for this abnormal Reformatzky product (29).

By condensation of 2,2′-diaminophenyl with a series of arylnitriles in molten 2-naphthalenesulfonic acid, the corresponding 6-aryldibenzo[*d,f*]-5,7-diazepines (LXXV) could be prepared (67).

Ketals (CXLII, R,R′ = alkyl, aryl) are formed from 2,2′-dihydroxybiphenyl and various ketones upon treatment with phosphorus pentoxide (188a). Treatment of 2,2′-dihydroxybiphenyl with thiophosgene gives CXLII (R, R′ = S) (188a).

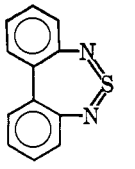


CXXXIX CXXXIXa CXL CXLa



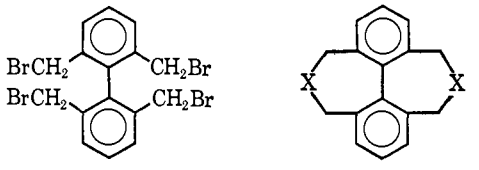
CXLI CXLII CXLIII

Reaction of 2,2′-diaminobiphenyl with a series of ethyl orthoesters affords 6-substituted dibenzodiazepines (LXXV). The cyclization was said to proceed *via* the 6-ethoxy-6-substituted dihydroazepines (146). The diazepinone CXLIII is formed by heating 2,2′-diaminobiphenyl and urea at 190–205° (134). Elaborating on this reaction, Ried and Sinharay cyclized 2,2′-diaminobiphenyl with a series of alkyl formimidate esters and obtained 6-substituted dibenzodiazepines (LXXV) (144). Further examples have also been reported by cyclizing substituted diamines with acids and formimidate esters (142, 143, 145, 146). 2,2′-Diaminobiphenyl has also been cyclized with thionyl chloride in refluxing toluene to give dibenzo[*c,e*][1,2,7]thiadiazepine (CXLIIIa) (50a), which upon heating loses sulfur to give benzo[*c*]cinnoline.

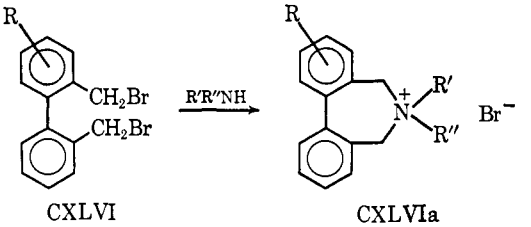


CXLIIIa

Dihydrooxepins can be formed by treating the appropriate 2,2′-bis(bromomethyl)biphenyl with silver oxide; for example, CXLIV can be doubly cyclized to CXLV (X = O) (121). The corresponding dihydrothiepin CXLV (X = S) is formed from CXLIV with sodium sulfide; cyclization with methylamine affords the N-methyldihydroazepin CXLV (X = NCH_3) (121). Reaction of CXLVI with a number of secondary amines gives the quaternary salts CXLVIa (73a). Condensation of the bis(bromomethyl) compound



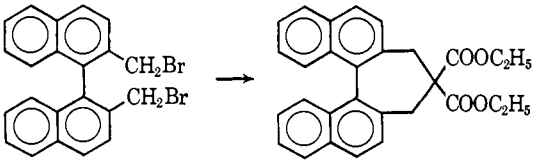
CXLIV CXLV
X=O, S, NCH_3



CXLVI CXLVIa

R = H, NO_2

CXLVII with diethyl malonate gives the cyclized diester CXLVIIa (122).



CXLVII CXLVIIa

III. CYCLIZATIONS BETWEEN AN *ortho*-BIPHENYL SUBSTITUENT AND THE OTHER RING

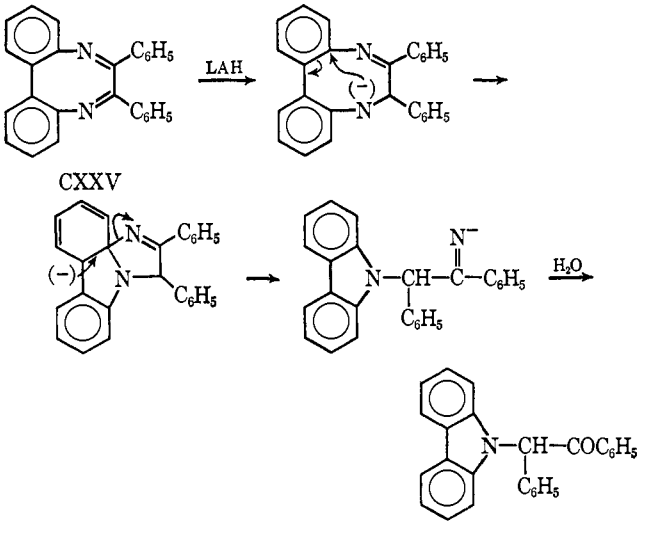
In addition to being capable of close steric approach to one another, each of the substituents of 2,2′-disubstituted biphenyls is capable of close approach to the *ortho* position of the other ring. As is shown in this

section, this latter fact facilitates intramolecuar aromatic substitution, electrophilic, nucleophilic, or homolytic.

The preparation of "several heterocyclic compounds" including carbazole from the reduction of 2,2′-dinitrobiphenyl with ferrous oxalate, carbon, or "other metals" was described in a patent some years ago (181). Carbazole and 2-aminobiphenyl were isolated from the reduction of 2-nitrobiphenyl with ferrous oxalate (161). Treatment of 2-nitrosobiphenyls (41) and 2-nitrobiphenyls (44) with triethyl phosphite (and triphenylphosphine in some cases) produced the corresponding carbazoles.

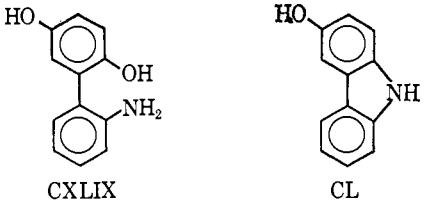
Reduction of the diazocine CXXV with lithium aluminum hydride gives the substituted carbazole CXLVIII in 63% yield (4). The probable mechanism, shown in Scheme VIII (4), involves an unexpectedly

SCHEME VIII



easy nucleophilic aromatic substitution which is greatly facilitated in these systems (*vide infra*).

Cyclization of 2′,5′-dihydroxy-2-biphenylamine (CXLIX) to 3-hydroxycarbazole (CL) can be accomplished both by ferric chloride and by hydrogenation with Raney nickel (166). The carbazole can also be formed by reduction of 2,5-dihydroxy-2′-nitrobiphenyl

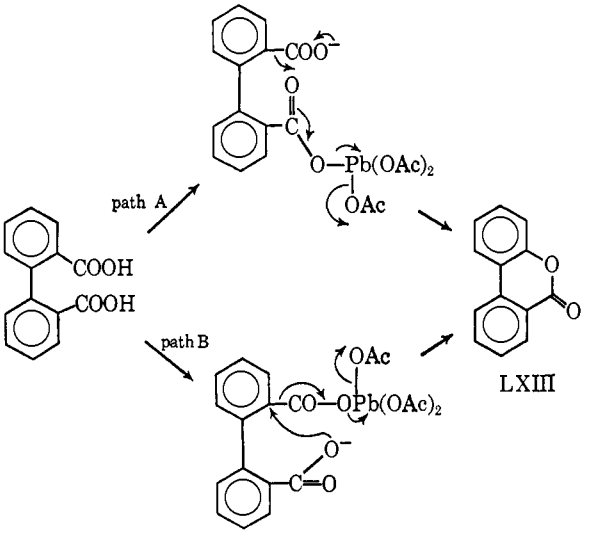


with Raney nickel (166a). According to the authors, the fact that such different conditions can accomplish the reaction is probably due to the possibility of redox reactions *via* the quinone form of CL, but this is difficult to rationalize considering the reductive conditions. A similar cyclization was accomplished by distilling a hydroxybiphenylamine with zinc dust (69a).

Oxidation of 2-biphenylcarboxylic acid gives 3,4-benzocoumarin (LXIII) under a variety of conditions including peroxide and peracid, chromic anhydride, and electrolysis (93). The reaction is probably a case of intramolecular homolytic aromatic substitution.

Reaction of diphenic acid with lead tetraacetate in pyridine–acetonitrile gives 3,4-benzocoumarin (LXIII) in 50% yield. Pyridine appears to be essential; substitution of triethylamine fails to give the reaction. Of the two mechanisms discussed, the authors favored path A (Scheme IX) because they felt electrophilic

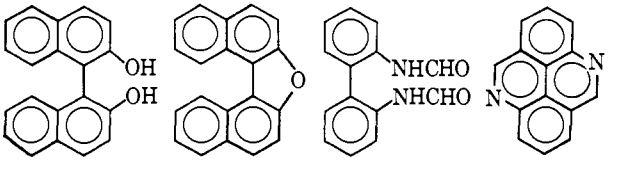
SCHEME IX



aromatic substitution should be favored over nucleophilic aromatic substitution (125). It would seem, however, that the latter cannot be so easily dismissed (*vide infra*). Prior decarboxylation is excluded because benzoic and phthalic acids are stable under the reaction conditions (125).

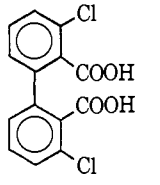
Treatment of 2,2′-dihydroxy-1,1′-binaphthyl (CLI) with nitrogen pentoxide affords the dinaphthylfuran CLII in 51% yield (48). This constitutes intramolecular displacement of a hydroxyl group, a most unusual reaction which is particularly facile in this series because of spacial proximity.

Cyclization of N-acyl-2-biphenylamines to give phenanthridines is well covered elsewhere (177) and will not be discussed here. The usual reagent is phosphorus oxychloride (Morgan–Walls synthesis) (177), but an aluminum chloride–sodium chloride melt (250–280°)

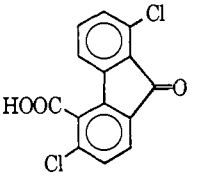


is required to cyclize 2,2′-diformylaminobiphenyl (CLIII) to 4,9-diazapyrene (CLIV) (12).

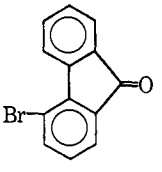
Treatment of 2-biphenylcarboxylic acids with acid gives the corresponding fluorenones. Thus CLVI is formed from CLV (84–86) and CLVII and CLVIII from the corresponding 2-biphenylcarboxylic acids (68, 119), the former in quantitative yield (119). Other facile conversions to substituted fluorenones have been noted (11a).



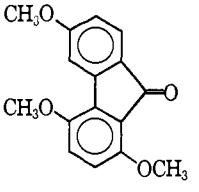
CLV



CLVI



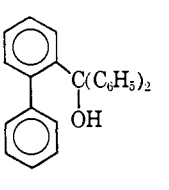
CLVII



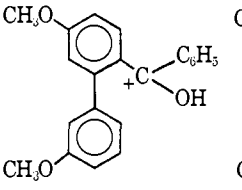
CLVIII

Heating 2,2′-diaminobiphenyls in aqueous hydrochloric acid (100, 114, 168) and sulfuric acid (46) gives good yields of the corresponding carbazoles; it was later found that phosphoric acid is a better reagent (101). Analysis of benzidine rearrangement products of several polycyclic hydrazobenzenes showed that carbazoles accompanied *o*-benzidines (and were probably formed from the latter), sometimes in comparable yields (15–19). All attempts to make the chloride from the triarylcarbinol CLIX resulted in cyclization to 9,9-diphenylfluorene (47). The rate-determining step of the cyclization, in acid, depends on substitution (74a). Other cyclizations have been observed (*cf.* ref 72a; ref 74a, footnotes 1–6). Several similar cyclizations were described in the same paper. Room-temperature reaction of 3,3′-dimethoxybiphenyl with benzoyl chloride in stannic chloride gave the cyclized fluorenol CLXI, which was presumed to form *via* the intermediate carbonium ion CLX (45). The acid chloride CLXII cyclizes spontaneously as formed to the corresponding fluorenone (69). Cyclization to 9,10-diphenylphenanthrene occurs when CLXIII is treated with acid (35a).

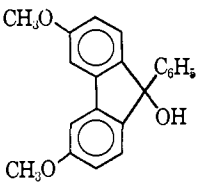
Treatment of the diazonium solution from 2,2′-diaminobiphenyl with cuprous bromide gives a mixture of benzo[*c*]cinnoline, carbazole, and 2,2′-dibromobiphenyl, the first predominant. Reversal of addition gives carbazole predominantly, the dibromide being a minor constituent in both cases (58). These results are at variance with a later report that the dibromide is the major product (79). Carbazole is formed from 2,2′-diaminobiphenyl by diazotization with cuprous chloride (134).



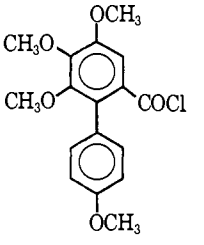
CLIX



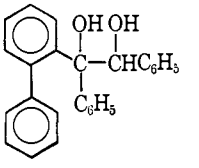
CLX



CLXI

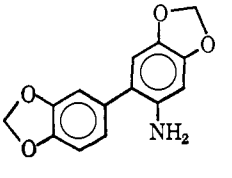


CLXII

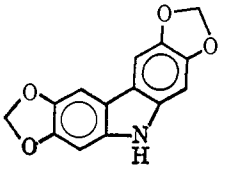


CLXIII

Cyclization to the substituted carbazole CLXIVa occurs when the diazonium solution from the oxygen-substituted 2-aminobiphenyl CLXIV is treated with potassium sulfide. The reaction is also observed with several analogous amines (56). Similar treatment of



CLXIV

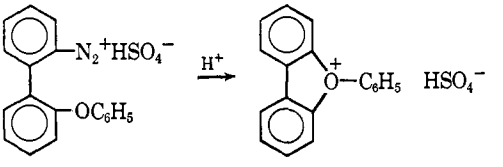


CLXIVa

2,2′-diaminobiphenyl gave carbazole (170).

Diazotization of monoacetyl-2,2′-diaminobiphenyl gives N-acetylcarbazole in 91% yield and 6-methyldibenzo[*d*,*f*]diazepine (LXXV, R = CH_3) in 3% yield (151).

Subsequent operations (heating or treatment with potassium iodide) with diazonium solutions of 2′-amino- (172), 2′-hydroxy- (113), and 2′-methoxy-2-biphenylamines (62, 113) afford good yields of dibenzofuran. An analogous cyclization, with retention of the substituent originally on oxygen, is observed upon heating the diazonium sulfate (CLXV) prepared *in situ* from 2′-phenoxy-2-biphenylamine, which gives CLXVa (131a). However, 6,6′-dimethyl-2,2′-diamin-

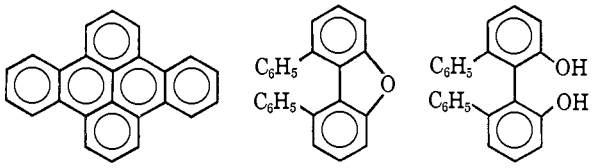


CLXV CLXVa

obiphenyl gives only the corresponding dihydroxy compound and no furan (152), probably because of coplanarity difficulties. Treatment of diazotized 2′-methoxy-2-biphenylamine with cuprous chloride in a carbon dioxide atmosphere yields 2-chloro-2′-methoxybiphenyl (113), so atmospheric oxygen is undoubtedly

involved in the cyclization. Diazotization of 2,2′-diamino-6,6′-diphenylbiphenyl gives dibenzopyrene (CLXVI), 4,5-diphenyldibenzofuran (CLXVII), and 2,2′-dihydroxy-6,6′-diphenylbiphenyl (CLXVIIa) in the yields indicated in Scheme X. The amount of

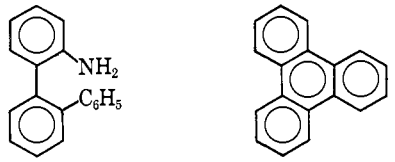
SCHEME X



CLXVI 100° 38% 15° 36% | CLXVII 30% 0% | CLXVIIa 5% 0%

ring-phenyl insertion product CLXVI was unaffected by the temperature (152).

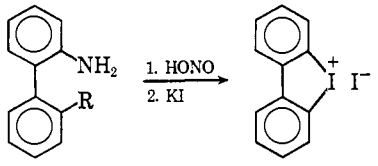
Similarly, it was noted that 2-amino-*o*-terphenyl (CLXVIII) underwent no intermolecular condensations when diazotized, but cyclized to triphenylene (CLXIX). The yield of CLXIX was found to be



CLXVIII CLXIX

better in acid (with or without copper) than with copper at pH 11–13 (60).

When 2,2′-diaminobiphenyl is diazotized and treated with potassium iodide, the iodonium iodide CLXX is formed along with some carbazole and 2,2′-diiodobiphenyl (109, 110). Several other 2′ groups are displaced to give the same product (109).

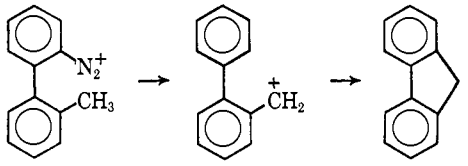


CLXX

R = NH_2, NO_2, Cl, Br, I, OCH_3

Carbazole formation was accomplished by heating a 2,2′-dimethoxybiphenyl with alcoholic ammonia in a sealed tube (33a).

Ring to methyl cyclization to give fluorenes has been observed for several 2-amino-2′-methylbiphenyls upon diazotization (107, 108, 111, 112, 175). General conclusions established were that cyclization is facile for 6,6′-unsubstituted compounds, difficult for 6-monosubstituted compounds, and impossible for 6,6′-disubstituted compounds because of the additional steric hindrance (107). The mechanism has been interpreted as ring substitution by a cation (CLXXI) rather than a radical (50).



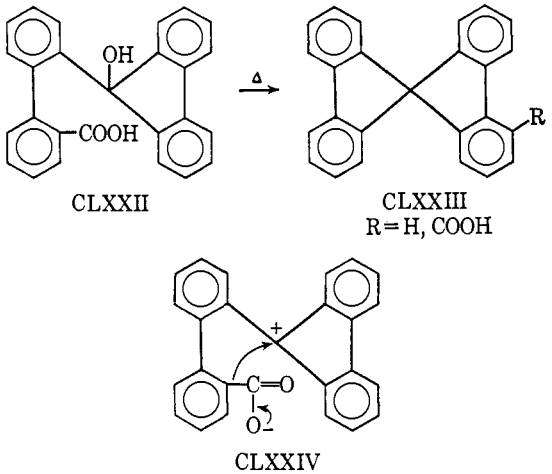
CLXXI

The bislactam of 6,6′-diaminobiphenyl-2,2′-dicarboxylic acid (LXXII) upon heating with barium hydroxide gives carbazole in 69% yield (156). This is probably a case of nucleophilic aromatic substitution, although this supposition should be checked by submitting 2,2′-diaminobiphenyl (the intermediate hydrolysis and decarboxylation product of LXXII) to the same conditions.

Although the amide of 2-biphenylcarboxylic acid undergoes cyclization to phenanthridone in 40% yield when subjected to treatment with potassium amide in *t*-butylamine, the reaction fails for diphenic acid mono- and diamides and secondary amides of 2-biphenylcarboxylic acid (93a).

Pyrolysis of 2,2′,6,6′-biphenyltetracarboxylic acid with lime gives fluorenone (117).

Pyrolysis of the alcohol–acid CLXXII at 220° gave a mixture of the spiro compounds CLXXIII (R = H, COOH) (77). The authors propose intramolecular acid catalysis for dehydration which makes cyclization of the intermediate carbonium ion CLXXIV by loss of CO_2 competitive with displacement of the 6-hydrogen atom.



CLXXII CLXXIII R=H, COOH

CLXXIV

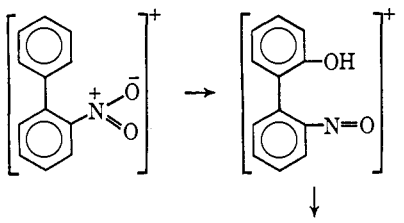
Cyclization of 2′-nitrobiphenyl-2-carboxylic acid to 3,4-benzocoumarin occurs by heating the former in quinoline or in tetralin in the presence of piperidine, or by heating the neat potassium salt (76). This is one of the most facile nucleophilic displacements known (see ref 39 for others), and this facility is attributed to the proximity of the reacting groups (76). Attack at the 1 position followed by a 1,2 shift is ruled out by the

observation that 4-nitrobiphenyl-2′-carboxylic acid is inert under these conditions (76).

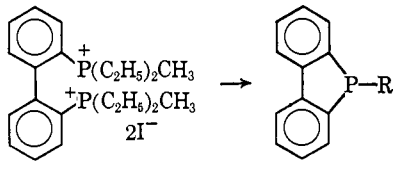
Pyrolysis of diphenic acid (or the anhydride) gave fluorenone in good yield (87).

In the course of discussing a rationale for mass spectral peaks corresponding to sequential loss of 2 moles of carbon monoxide in the mass spectrum of 2-nitrobiphenyl, Meyerson, Puskas, and Fields postulate oxygen transfer to the unsubstituted ring as the primary decomposition step (Scheme XI). Prior observations of such a transfer for 1-nitronaphthalene (28) are cited as precedent (118).

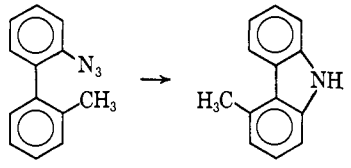
SCHEME XI



The phosphazoles CLXXVI (R = CH_3, C_2H_5) are formed upon heating the diphosphonium salt CLXXV. This was described as the first such cyclization in phosphorus chemistry (3).



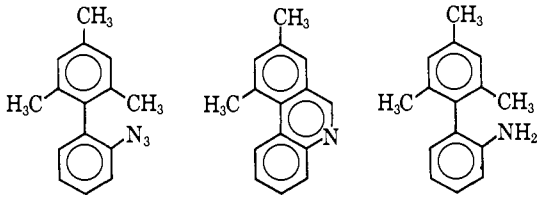
CLXXV CLXXVI



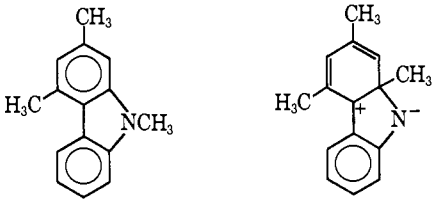
CLXXVII CLXXVIII

Either pyrolysis or photolysis of 2-azidobiphenyl gives carbazole in virtually identical yields (76 *vs.* 77%) (159). In the course of studying nitrenes at low temperatures, Reiser and Frazer noted that several arylnitrenes are stable at 77°K, but 2-biphenylylnitrene cyclizes to carbazole even at that low temperature (141). Pyrolysis of 2-azido-2′-methylbiphenyl (CLXXVII) yields 4-methylcarbazole (CLXXVIII), but only tars are obtained by either pyrolysis or photolysis of 2,2′-diazido-6,6′-dimethylbiphenyl (49). Also, photolysis of 2,2′-diazidobiphenyl gives neither carbazole nor benzo[*c*]cinnoline (81).

Pyrolysis of 2′-azido-2,4,6-trimethylbiphenyl (CLXXIX) at 230° gives the corresponding phenanthridine CLXXX, amine CLXXXI, and the N-methylcarbazole CLXXXII in 50, 30, and 5% yields, respectively. It is proposed that CLXXX is formed *via* the dihydro compound by insertion into the methyl group, and that CLXXXII is formed from CLXXXIII (or the corresponding diradical) (162). A study of



CLXXIX CLXXX CLXXXI

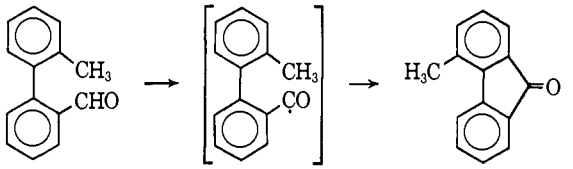


CLXXXII CLXXXIII

several suitable compounds showed that only methyl group insertion was observed in the foregoing reaction; methoxyl insertion was never observed (163).

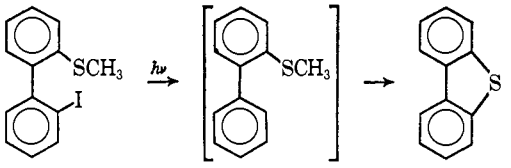
Pyrolysis of the disilver salt of diphenic acid yields 3,4-benzocoumarin and biphenyl (no yields given) (59).

When 2-formyl-2′-methylbiphenyl (CLXXXIV) is treated with *t*-butoxy radicals, cyclization to 4-methylfluorenone (CLXXXV) occurs probably *via* the formyl radical CLXXXVI. The facility of the reaction was attributed to steric proximity (82).



CLXXXIV CLXXXVI CLXXXV

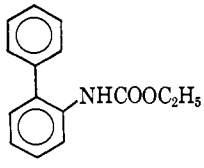
Irradiation of 2-iodo-2′-methylthiobiphenyl (CLXXXVII) in benzene gives dibenzothiophene in quantitative yield (92). Iodine is also formed in 82% yield, and presumably the third product is the methyl radical, for toluene is formed in 37–45% yield. The authors note that this is the first example of radical displacement on the sulfur atom of a sulfide and that the



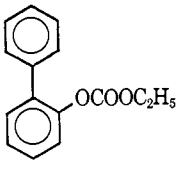
CLXXXVII CLXXXVIII

reaction probably involves the radical CLXXXVIII. The same cyclization occurs when CLXXXVII is reduced with tributyltin hydride in the dark (92).

Molecular orbital calculations have indicated that there is localization of electron density in the *ortho* positions of stilbene in the excited (photoinduced) state. This is also apparently the case with photoexcited biphenyls, for irradiation of ethyl N-2-biphenylylcarbamate (CLXXXIX) gives phenanthridone in 85% yield, and irradiation of ethyl 2-biphenylyl carbonate (CLXC) gives 3,4-benzocoumarin (LXIII), also in 85% yield (188).



CLXXXIX



CXC

ACKNOWLEDGMENTS.—We thank the Public Health Service, National Institutes of Health, for partial support of this work under Grants 5-F1-GM-21,702-04 and CA-02551. One of us (R. E. B.) thanks his wife for assistance in preparing the manuscript including typing and proofreading. The authors thank Mrs. E. Cantu for typing the final manuscript.

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