THE ULLMANN SYNTHESIS OF BIARYLS

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CONTENTS

I. INTRODUCTION

A general method for the preparation of a biaryl consists in the condensation of two molecules of an aromatic halide in the presence of a metallic agent, with the elimination of metal halide:

$$RX + R'X + M \longrightarrow RR' + MX_2$$

The work of Fritz Ullmann (216, 219) and of subsequent investigators showed that copper is particularly effective in this type of condensation,[2] so that biaryl formation with the elimination of copper halide has come to be known as the Ullmann reaction.

The synthesis devised by Ullmann is of quite general applicability and has found wide use in the preparation of many symmetrical and unsymmetrical biaryls and polyaryls which would otherwise be difficult to obtain.

[1] Abbott Laboratories Fellow, 1943–44. The author is indebted to Dr. Robert B. Carlin for assistance in the preparation of the manuscript.

[2] The relative merits of various metals in this condensation are discussed in Houben's *Die Methoden der organischen Chemie*, Vol. II, pp. 786–800, Georg Thieme, Leipzig (1925), and in references 64 and 152.

II. NATURE AND SCOPE OF THE REACTION

A. The aromatic halide

The success of the Ullmann reaction is dependent upon the nature of the aromatic halide. Considering first the halogen residue, it has been observed that chlorine, bromine, iodine, and the halogenoid thiocyanate group (97) may be eliminated with biaryl formation. Closely related is the elimination of the disulfide linkage (97), according to the equation:

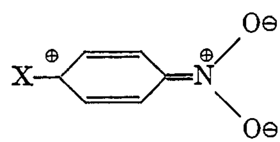
$$RSSR + Cu \longrightarrow RR + CuS$$

An aromatic fluorine atom has never been reported to be active in the Ullmann reaction.

The order of reactivity of the halogens is I>Br>Cl. In general, the latter two substituents undergo reaction only when activating groups are present in the aromatic nucleus. The amount of activation required in order that the Ullmann reaction may occur has been studied with a great variety of halogenated aromatic compounds by Mascarelli (132).

Substituents in the aromatic nucleus which affect the Ullmann reaction of halogenated benzene derivatives may be divided into four classes:

(*1*) *Activating groups:* Certain electronegative groups in the ortho- and para-positions with respect to the halogen atom activate the latter through the operation of a $-T$ effect[3] which leaves the carbon atom to which the halogen is attached with a residual positive charge. The nitro group is the most effective activator:



I

An ortho or para carbalkoxyl group or carbonyl group also activates markedly. Numerous examples of $-T$ activation by these groups may be found in table 1. Substituents such as an ortho halogen atom which might be expected to activate in a similar manner through the operation of a $-I$ effect actually have no detectable influence on reactivity. Thus 2,4,6-trichloroiodobenzene undergoes the Ullmann reaction no more readily than does iodobenzene (216).

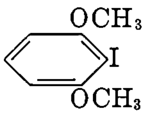
(*2*) *Deactivating groups:* Substituents which exert a $+T$ effect would be expected to lead to deactivation when they occupy positions ortho or para to the halogen atom. Evidence for this effect is not clear-cut (16, 216).

(*3*) *Inhibiting groups:* A decrease in yield of biaryl is generally observed when certain groups are present in the aromatic nucleus (216). Inhibition is particularly marked when groups such as $—NH_2$, $—NHCOCH_3$, $—NHCH_3$, $—SO_2NH_2$, $—SO_2NHC_6H_5$, —COOH, and —OH, which can give rise to amination, decarboxylation, or ether formation as a side reaction, are present. The nitrogen-

[3] The terminology used here is that of Remick, *Electronic Interpretations of Organic Chemistry*, John Wiley and Sons, Inc., New York (1943).

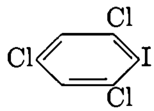
containing groups must be protected by alkylation or acylation, the carboxyl group by esterification, and the hydroxyl group by etherification.

(*4*) *Steric effects:* In some cases bulky substituents in positions adjacent to the reactive halogen hinder biaryl formation. The relative hindrance of these groups in the Ullmann reaction is the same as their interference effect on the restriction of rotation in resolvable biphenyls.[4] For example, the yields of biaryl indicated were obtained from the following iodobenzene derivatives: 2,6-dimethoxyiodobenzene (II) (229), 2,4,6-trichloroiodobenzene (III) (216), and 2,4,6-trimethyliodobenzene (IV) (145, 216).



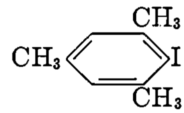
II

(yield of biaryl 85–90%)



III

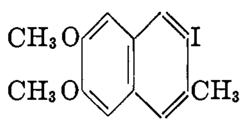
(yield of biaryl 52.5%)



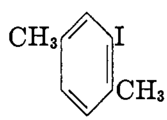
IV

(yield of biaryl very poor)

In other cases the effect is not predictable. Thus V could not be caused to undergo an Ullmann reaction under a variety of conditions (3), while a 90 per cent yield of the expected biaryl was obtained with VI (216).



V



VI

The generalizations regarding the effect of substituents on the Ullmann reaction of benzene derivatives may be applied to other aromatic compounds according to the usual concepts of aromaticity.

B. Synthesis of unsymmetrical biaryls[5]

The Ullmann reaction has been applied with considerable success to the synthesis of unsymmetrical biaryls. In addition to a consideration of the previously discussed conditions, the synthesis of an unsymmetrical biaryl requires the selection of an optimum ratio of the two component starting materials. By making certain simplifying assumptions, the conditions which are necessary for a successful crossed reaction can be deduced.

When a mixture of two aromatic halides, RX and R′X′, is subjected to the conditions of the Ullmann reaction, four competing reactions are possible:

$$RX + RX \longrightarrow R\text{—}R \qquad (1)$$

$$RX + R'X' \longrightarrow R\text{—}R' \qquad (2)$$

$$R'X' + RX \longrightarrow R'\text{—}R \qquad (3)$$

$$R'X' + R'X' \longrightarrow R'\text{—}R' \qquad (4)$$

[4] For references to the original literature see Shriner, Adams, and Marvel in *Organic Chemistry, an Advanced Treatise*, edited by Henry Gilman, Second Edition, Vol. I, p. 362, John Wiley and Sons, Inc., New York (1943).

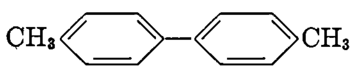
[5] For a discussion of other methods of synthesis of unsymmetrical biaryls see Bachmann and Hoffmann, *Organic Reactions*, edited by Roger Adams, Vol. II, pp. 241–3, John Wiley and Sons, Inc., New York (1944).

Depending upon the relative rates of these four reactions, a number of different courses for the over-all reaction may be deduced:

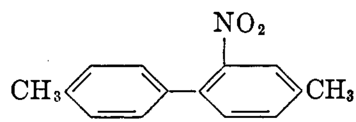
Case 1: The four reactions proceed at nearly equal rates. If this is true and equimolar quantities of the two component starting materials are used, the yield will be distributed among the various possible products approximately as follows:

$$\underset{(1\text{ mole})}{RX} + \underset{(1\text{ mole})}{R'X'} \longrightarrow \underset{(\frac{1}{4}\text{ mole})}{RR} + \underset{(\frac{1}{2}\text{ mole})}{RR'} + \underset{(\frac{1}{4}\text{ mole})}{R'R'}$$

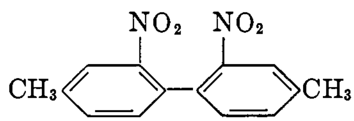
The success of the reaction depends upon the feasibility of separating the desired product from the symmetrical biaryls. This may be accomplished if the chemical or physical properties of the biaryls differ sufficiently. For example, Marler and Turner (123) subjected a mixture of 4-iodotoluene and 4-bromo-3-nitrotoluene to the conditions of the Ullmann reaction and obtained a mixture of the biphenyls VII, VIII, and IX.



VII



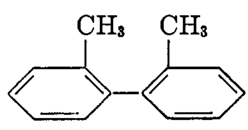
VIII



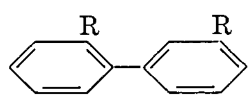
IX

VII and VIII were separated from the dinitrobiphenyl IX by extraction with petroleum ether, after which VII and VIII were separated by fractional distillation.

A much more difficult case was encountered by Mayer and Freitag (136), who obtained the biphenyls X, XI, and XII by the Ullmann reaction of 2-iodo- and

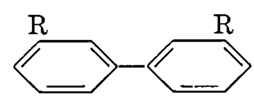


X



XI: R = CH_3

XIII: R = COOH

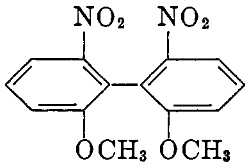


XII: R = CH_3

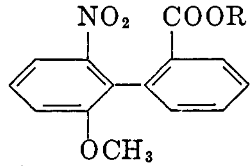
XIV: R = COOH

3-iodotoluenes. Biphenyl X was separated from the mixture of products by repeated fractional distillation. The remaining mixture of XI and XII was oxidized to give a mixture of the corresponding diphenic acids XIII and XIV, which were separated by extraction with water.

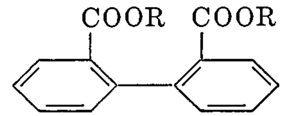
A difference in the number of polar groups provides a basis for a chemical separation. For example, Adams and Finger (2) obtained a mixture of the biphenyls XIV, XV, and XVI as the product of a crossed Ullmann reaction.



XIV



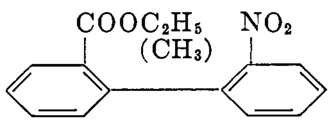
XV: R = CH_3
XVII: R = H



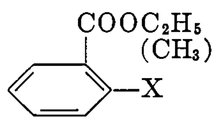
XVI: R = CH_3
XVIII: R = H

After saponification with sodium hydroxide solution, the neutral compound XIV was separated from a mixture of the sodium salts of the acids XVII and XVIII. Finally, the two acids were separated by fractional crystallization from benzene.

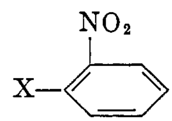
Case 2: Reaction 1 proceeds at a rapid rate compared to reactions 2, 3, and 4. In this case RX would be completely used up in the formation of RR. When the reaction is continued for a longer time or under more drastic conditions, R′X′ reacts to give R′R′. The symmetrical biaryls are the only products of the reaction. In such a case the formation of RR′ may be favored by changing either X or X′ in the starting materials, so that the aromatic halides are of more nearly equal reactivity. For example, the synthesis of XIX from XX and XXIII was accomplished in 20 per cent yield (156), while a 68 per cent yield was attained by the use of XXII and XXI (184a).



XIX



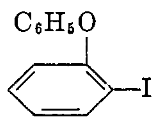
XX: X = Br
XXII: X = I



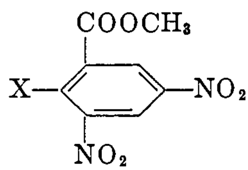
XXI: X = Br
XXIII: X = I

In the latter case the two components are of more nearly equal reactivity, since the lower activity of bromine as compared to iodine is compensated by the greater activation effect of the nitro group as compared to the carbalkoxyl group.

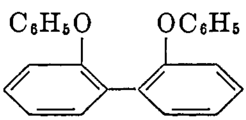
However, the same principle was unsuccessful when applied to the attempted preparation of biphenyl XXVIII (111).



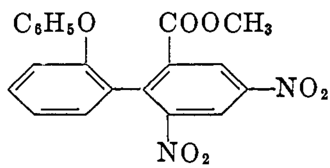
XXIV



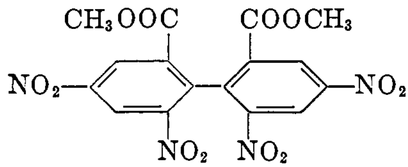
XXV: X = Cl
XXVI: X = Br



XXVII



XXVIII

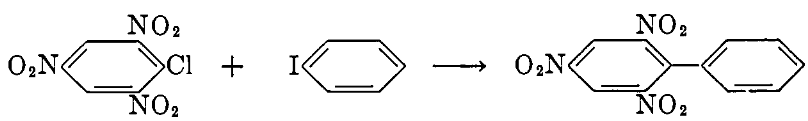


XXIX

In this case a reaction mixture containing XXIV and XXV gave only the symmetrical biphenyl XXVII. When the bromo derivative XXVI was used in the reaction instead of the chloro derivative, with the intention of making the reactivities of the two components more nearly equal, the reactivity of the dinitrocarbomethoxy nucleus was actually increased to such an extent that XXIX was the only product which could be isolated and again no unsymmetrical biphenyl was formed.

Another condition which favors unsymmetrical biaryl formation is the presence of an excess of the less reactive component. Numerous examples of the use of this technique are to be found in the literature (5, 67, 113, 155a).

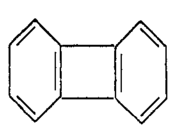
Case 3: Reaction 2 or reaction 3 predominates. Most of the reactants are utilized in the formation of RR′, and relatively small amounts of the symmetrical biaryls are formed. In the most favorable cases the crossed reaction may be obtained with the complete exclusion of symmetrical products (110). An example of this case which has been carefully investigated (155a) is the reaction of picryl chloride and iodobenzene to give 2,4,6-trinitrobiphenyl as the only detectable product.



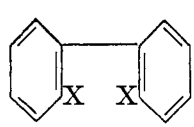
XXX Picryl chloride — XXXI Iodobenzene — XXXII 2,4,6-Trinitrobiphenyl

C. Intramolecular reactions

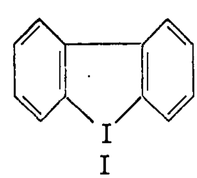
Several intramolecular Ullmann reactions have been described in the literature. Lothrop has reported (120, 121) the synthesis of biphenylene (XXXIII) and several of its derivatives by the treatment of appropriately substituted



XXXIII
Biphenylene



XXXIV

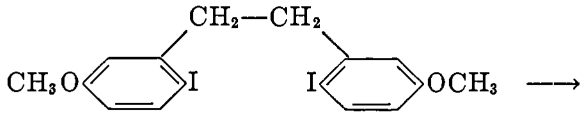


XXXV

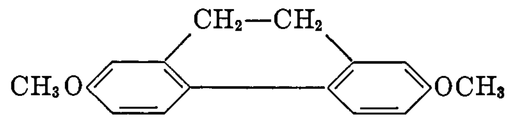
2,2′-dihalogen biphenyls (XXXIV) or 2,2′-biphenyleneiodonium iodides (XXXV) with cuprous oxide.

The preparation of 2,7-dimethoxy-9,10-dihydrophenanthrene (XXXVII)

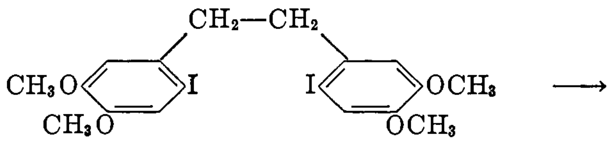
(43) and of 2,3,6,7-tetramethoxy-9,10-dihydrophenanthrene (XXXIX) (54) was accomplished by intramolecular Ullmann reactions involving the appropriately substituted dibenzyl derivatives XXXVI and XXXVIII.



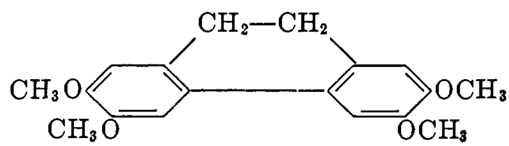
XXXVI



XXXVII

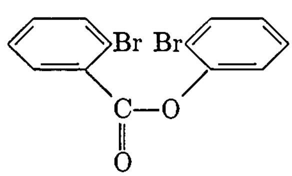


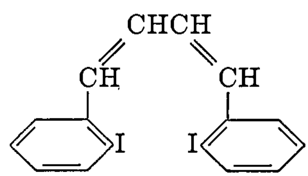
XXXVIII



XXXIX

Cahn (32) was unable to effect an intramolecular Ullmann reaction of 2-bromophenyl 2-bromobenzoate (XL).

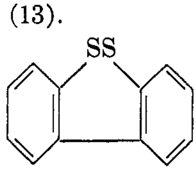


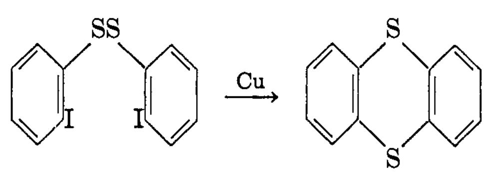


XL XLI

The attempted intramolecular Ullmann reaction of 2,2′-diiododistyryl (XLI) was also unsuccessful (153).

A good yield of thianthrene (XLIc) was obtained as the product of the attempted synthesis of the cyclic disulfide XLIa from di-*o*-iodophenyl disulfide (XLIb) (13).

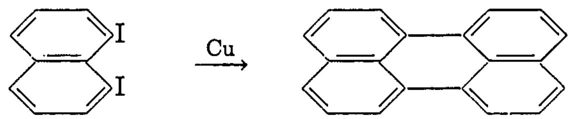




XLIa XLIb XLIc

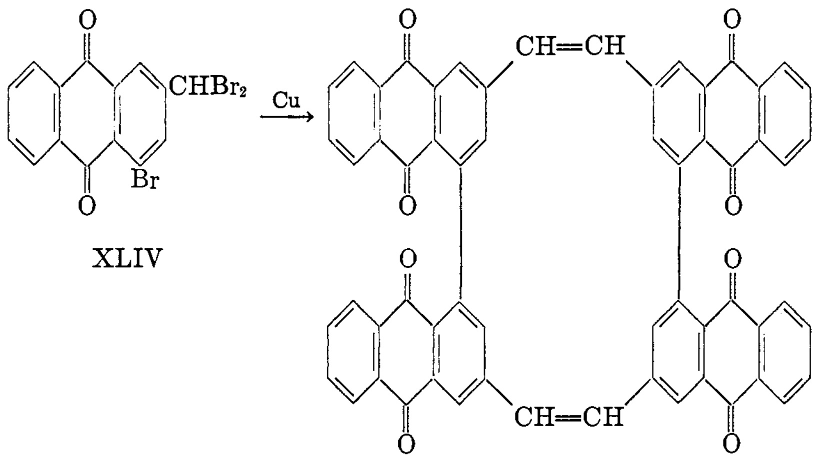
D. Reactions of polyfunctional compounds

Cyclic products may also be obtained when polyhalogenated aromatic compounds are subjected to the conditions of the Ullmann reaction. The synthesis of perylene (XLIII) from 1,8-diiodonaphthalene (173a) is an example of such a reaction.



XLII 1,8-Diiodonaphthalene — XLIII Perylene

Similarly, XLIV has been reported to form XLV (155).



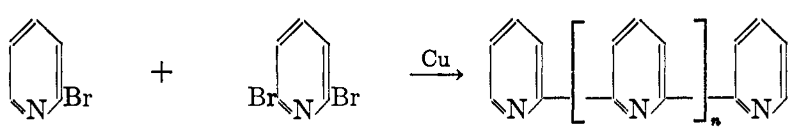
XLIV

XLV

Sircar and Majumdar (186) have reported that a tetraphenylene, presumably cyclic, is obtained when 4,4′-diiodobiphenyl is subjected to the conditions of the Ullmann reaction.

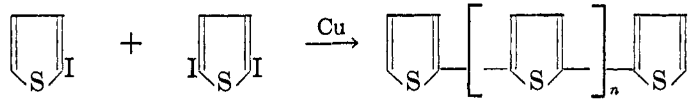
Attempts to prepare biphenylene (XXXIII) by reactions of the polyfunctional type were unsuccessful. When either 2-bromoiodobenzene (126) or 1,2-diiodobenzene (49) was heated with copper powder, only resins were obtained.

The reaction of a mixture of polyfunctional and monofunctional compounds may yield a mixture of low polymers. Thus, Burstall (28) obtained a mixture of di-, tri-, and tetra-pyridyls by the reaction of 2-bromopyridine and 2,6-dibromopyridine.



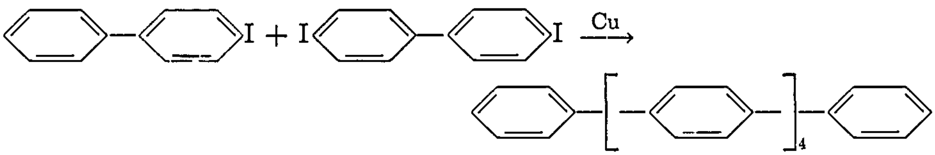
2-Bromopyridine 2,6-Dibromopyridine (n = 0, 1, 2)

The same technique was used by Steinkopf and his coworkers (201, 205) in the preparation of polythienyls.



(n = 1, 2, 3, 4, 5)

Pummerer and Seligsberger (152) made use of the same principle in the preparation of sexiphenyl.



Sexiphenyl

III. EXPERIMENTAL CONDITIONS

The experimental technique employed in carrying out the Ullmann reaction is simple. In general, the aromatic halide is maintained at a suitable temperature in an open tube or flask while finely divided copper is added. In certain cases various special precautions must be observed.

A. Starting materials

As far as can be determined by an examination of the literature, the organic halides used in the Ullmann reaction in general need not be specially purified.

On the other hand, the nature of the copper used in the reaction has been the subject of considerable discussion and controversy. Commercial pulverized copper, known also as copper bronze, has long been one of the most commonly employed forms of the metal. Frequent reference is made to a particular brand of copper bronze known as "Naturkupfer C", which was obtainable from Bernhard Ullmann and Co. of Fürth (215, 216).

Freshly precipitated copper has also been used successfully (22). This is prepared by the treatment of zinc dust with copper sulfate solution, followed by washing with alcohol and ether and drying. However, Ullmann and Bielecki (219) and also Schreiner (178) observed that the mechanically pulverized copper bronze is preferable to the chemically precipitated or so-called molecular copper.

Commercial copper bronze contains traces of oil which is used during its preparation. This impurity is readily removed by washing with ligroin or ether, but Ullmann and Bielecki (219) observed that preliminary treatment is unnecessary when the copper is to be used in the biaryl synthesis. On the other hand, Kleiderer and Adams (95) recommend activation of copper bronze by treatment with iodine in acetone, followed by washing with hydrochloric acid and acetone and drying in a desiccator. They state that whereas ordinary copper bronze sometimes gives poor results in the Ullmann reaction, this simple treatment insured more uniform results and frequently made possible a more rapid reaction at a lower temperature.

Müller and Tietz observed (146) that when methyl 3,5-dichloro-4-iodobenzoate was treated with Naturkupfer C which had been reduced in hydrogen at 250–300°C., the hydrogen retained by the copper effected a partial reduction to methyl 3,5-dichlorobenzoate, with a consequent lowering in the yield of the desired biphenyl derivative. An improved yield was obtained when they used "Naturkupfer purified in nitrogen."

Lothrop (120, 121) found that cuprous oxide was effective in the synthesis of biphenylene from 2,2′-dihalogen biphenyls or 2,2′-biphenyleneiodonium iodide, while pure copper metal was without effect.

In the experience of the author (33a, 210a), Baker's precipitated copper powder has been found to be quite satisfactory for use without preliminary treatment. "Gattermann's precipitated copper powder" has been reported (155b) to be more active than the best copper bronze.

B. Proportions of reacting substances

A generous excess of copper is always used in the Ullmann reaction. Three times the theoretically required quantity is frequently employed, although two or three times that amount may be used for small batches when less reactive organic halides are being subjected to the reaction.

Since the reaction is often vigorously exothermic, only a small portion of the requisite amount of copper is placed in the reaction mixture at the outset, and the remainder of the metal is added in small portions during the course of the reaction.

C. Temperature

The temperature employed in the Ullmann reaction varies from 100° to 360°C., depending upon the reactivity of the aromatic halide.

In the case of any particular reaction, two temperatures are of importance: (*1*) the temperature at which reaction occurs at a reasonable and controllable rate; (*2*) the maximum temperature to which the reaction mixture may be subjected without causing the occurrence of undesirable side reactions or decomposition. For example, reactions of compounds containing the nitro group must not be carried out at a temperature exceeding 240°C.; otherwise reduction of the nitro groups by the copper may occur (61).

The desired temperature may usually be most conveniently maintained by immersing the reaction vessel in a heated metal bath. The use of two thermometers, one immersed in the metal bath and the other directly in the reaction mixture, is desirable. In the case of small-scale reactions, the latter thermometer may also be employed as a stirring rod.

The optimum reaction temperature is probably that at which the gradual addition of the copper suffices to maintain an observable yet readily controllable exothermic reaction. In the case of reactive halides, the evolution of heat may serve to keep the reaction mixture at a temperature 5° to 20°C. above that of the bath. Toward the completion of the reaction less heat is evolved, and the temperature of the bath must be increased. A temperature somewhat higher than the optimum reaction temperature is usually maintained for some time after all of the copper has been added and the observable reaction has subsided. Long-continued heating in this manner probably serves no useful purpose (92).

The reaction temperature of low-boiling compounds can sometimes be attained only by the use of a sealed tube or bomb (10, 36, 136, 167, 216).

In most cases the reaction may be carried on successfully over a considerable range of temperature, while in other cases the temperature control appears to be extremely critical (226).

D. Diluents

The violence of the reaction which occurs when very reactive halides are used in the Ullmann reaction may be moderated by the use of a diluent. The following organic substances have been used for this purpose: nitrobenzene, toluene, naphthalene, *p*-cymene, biphenyl, and anthracene. Sand has also been employed (61, 219), even when its use was probably superfluous (105). The chief purpose of sand in the reaction mixture in large-scale runs is to assist in breaking up and extracting the soluble material from the hard mass which is usually produced.

Substitution of a hydrogen atom for the aromatic halogen occurred when tetralin was used as a diluent (69, 111).

An aqueous solution of copper sulfate has been used as a diluent in the Ullmann reaction of certain halogenated aromatic sulfonates (13, 46).

E. Protective atmosphere

The Ullmann reaction is sometimes conducted in an atmosphere of carbon dioxide, hydrogen, or nitrogen. It is not evident under what conditions this precaution is of value, but in at least one reported case (70) a definite improvement in yield was observed when nitrogen was used to protect the reactants from the air. Further examples of the use of a protective atmosphere are to be found in tables 1 and 2.

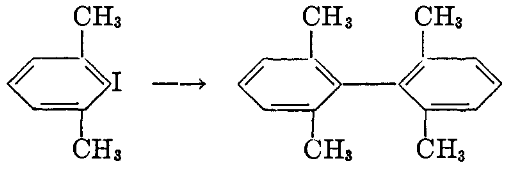
F. Agitation

As copper powder is added to the medium during the reaction, it rapidly settles to the bottom and must be stirred to expose the active surface of the metal. In the case of small-scale reactions employing 5 to 25 g. of material, a thermometer usually serves as a rod for intermittent manual stirring. In mechanical stirring of larger-scale batches, the paddle must be able to agitate the heavy sludge of spent copper which settles to the bottom of the vessel. In the case of reactions which must be carried out in a sealed tube or under a protective atmosphere, provision for rocking or rotating the vessel is advisable.

G. Isolation of products

The procedure used in isolating the products depends greatly upon the chemical nature of the substances obtained. The considerations which apply particularly to the unsymmetrical biaryls have been discussed in Section II B. The isolation procedure usually utilizes polar or reactive groups in the molecule.

Thus, products containing one or more carbalkoxyl groups are saponified and isolated as the corresponding carboxylic acids. In the preparation of biphenyl XLVII from 2,6-dimethyliodobenzene (XLVI) (33a), difficulty was experienced in separating the product from unchanged starting material. Treatment of the mixture with Raney nickel gave a readily separable mixture of the biphenyl and *m*-xylene.



XLVI XLVII

Further detailed procedures which are applicable to specific types of product are to be found in the literature cited in tables 1 and 2.

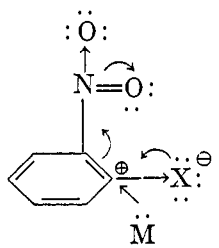
IV. MECHANISM

The mechanism of the Ullmann reaction is not known. However, by analogy with the reactions of other metals with organic halides, we might expect to find as intermediates either (*1*) free radicals, (*2*) organometallic compounds of moderate stability, or (*3*) metallic complexes of transitory existence.

The possibility of a free-radical mechanism has been suggested by Rapson and Shuttleworth (153a). They found that when iodobenzene was caused to react with copper in the presence of ethyl benzoate, the product after saponification contained 2- and 4-diphenylcarboxylic acids. It seemed probable that these products were the result of the formation by the iodobenzene and copper of a free phenyl radical which displaced a hydrogen atom from either the ortho- or the para-position of the ethyl benzoate. However, in all cases in which the Ullmann reaction has been carried out in the usual way, biaryl bond formation was observed to occur only at the carbon atom from which a reactive halogen atom had been displaced. Since the existence of a free-radical intermediate would be expected often to lead to a variety of products, it cannot be considered a plausible mechanism for the normal reaction. Because free radicals readily lead to polymerization, their occurrence as the result of a side reaction offers an explanation for the formation of polymers (201) or resinous materials which are sometimes obtained as by-products of biaryl formation.

The preparation and reactions of organocopper compounds have been studied by Gilman and Straley (63). They point out that although well-characterized RCu compounds are known to undergo coupling to yield RR compounds, it is not known whether an organocopper compound of this type is formed as an intermediate in the Ullmann reaction. An R_2Cu compound has also been suggested as a possible intermediate in the coupling reaction of RCu, but there is no experimental evidence for the existence of such a compound.

Any mechanism proposed for the Ullmann reaction must be in agreement with two facts: (*1*) the activity of a series of aromatic halides increases in the order $RCl < RBr < RI$; (*2*) activity is increased by $-T$ substituents in the ortho- and para-positions. The fact that these $-T$ substituents produce a residual plus charge on the ortho- and para-positions suggests that a nucleophilic attack by the metallic copper (M) at the activated position may be an initial and rate-determining step. The halogen atom (X) would contribute to the activation by the net result of a $-I$ and a $+T$ effect. The combination of these two



effects must be such that the polarization of the R—X bond increases in the order RCl < RBr < RI.

Further evidence for the participation in the reaction of an activated complex is the reaction referred to on page 144. In this case Rule and Smith (155a) observed that although iodobenzene (XXXI) does not react with copper below 220°C. and picryl chloride (XXX) reacts explosively at 135°C., equimolar quantities of the two react in nitrobenzene solution at 160–165°C. to give an 85 per cent yield of the unsymmetrical biphenyl XXXII. They conclude that, "In the presence of picryl chloride the relatively nonreactive iodobenzene undergoes some special form of activation, permitting it to enter into reaction at a temperature much below that at which it would ordinarily do so." In terms of activated complex formation, the copper–picryl chloride complex reacts preferentially with iodobenzene. Rule and Smith suggest that steric hindrance of the ordinarily more reactive halogen atom of picryl chloride is the controlling factor in this preferential reaction.

We may conclude that a possible mechanism for the reaction consists in two consecutive steps: (*1*) A nucleophilic reaction of copper with the aromatic halide to form an activated complex at the metal surface. The occurrence of this step is governed largely by the susceptibility of the aromatic halide to nucleophilic attack. (*2*) The reaction of the activated complex with a second molecule of aromatic halide to form a biaryl molecule plus copper halide. This reaction is governed to a greater extent by steric factors. A more detailed knowledge of the mechanism must await further experimentation.

V. TABLES

Symmetrical biaryls which have been prepared by the Ullmann reaction are listed in table 1. The compounds have been arranged, with a few exceptions, according to the familiar Beilstein system.

Unsymmetrical biaryls are listed in table 2. In cases where non-equimolar amounts of the reactants were used the yield of unsymmetrical product was calculated on the basis of the component present in lower molar concentration.

A number of examples of unsuccessful attempts to use the Ullmann reaction are presented in condensed form in table 3. This table is perhaps less complete than table 1 or 2.

The data were obtained by a systematic search of the literature up to and including the 1944 *Chemical Abstracts*.

TABLE 1

Symmetrical biaryls (RR) prepared by the reaction $2RX \xrightarrow{Cu} RR$

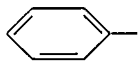
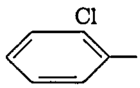
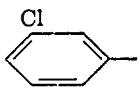
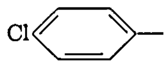
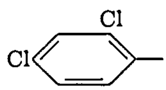
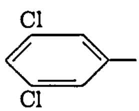
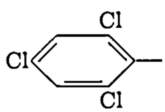
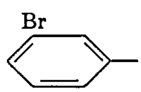
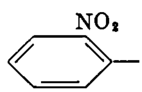
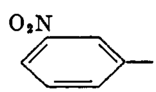
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	I	230	Sealed tube	82	(216)
	I	260			(227)
		150	Slow reaction		(132)
	Br	204	Slow reaction		(132)
	I	250		96	(226)
		250		67	(216)
		230	Slow reaction		(132)
	I	200–250		82	(216)
		226–227	Slow reaction		(132)
	I	200–270		53	(216)
	I				(230)
	I	220–230		52.5	(216)
	I			Poor	(216)
	Cl	210–245	With dry sand	60	(219)
		215–225	With dry sand	52–61	(61)
		240–245			(105, 106, 161)
	Br	230–240			(128)
		200–220		75	(219)
		185	Vigorous reaction		(132)
	I	134	Vigorous reaction		(132)
	X?	230			(157)
	I	210–225		26–52	(46, 161, 219)
		230	Moderate reaction		(132)
	Br	257	Slow reaction		(132)

TABLE 1—*Continued*

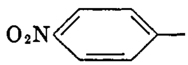
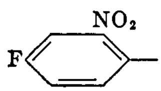
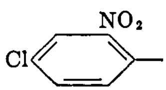
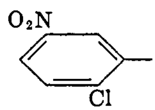
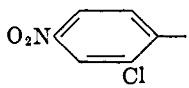
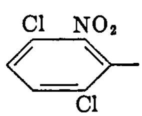
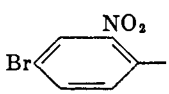
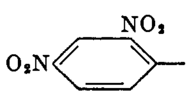
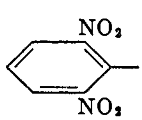
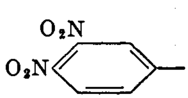
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	I	220–235		52	(219)
		287	Slow reaction		(132)
	Br	255	Slow reaction		(132)
	Br	240–250		46	(184)
	Cl	240–255		42	(219)
		240–245			(106)
	I	138	Rapid reaction		(132)
	I				(37a)
	I				(37a)
	I				(244)
	Br	190–225		65	(105, 219)
		210			(106)
	Cl		Boil in $C_6H_5NO_2$	60	(106, 219, 227)
		295	Violent reaction		(132)
	Br	157	Rapid reaction		(132)
			Boil in $C_6H_5NO_2$	65	(219)
	Cl		Boil in $C_6H_5NO_2$		(20)
	I	230–250		47	(219, 36a)

TABLE 1—*Continued*

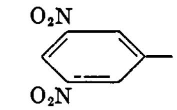
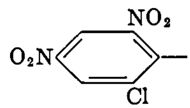
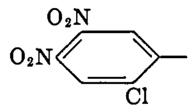
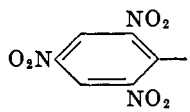
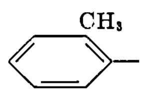
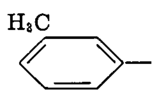
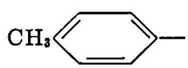
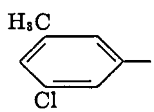
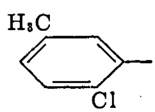
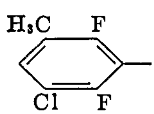
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	I	270		15	(36)
	I	240		46	(37a)
	I		Boil in $C_6H_5NO_2$	41	(37a)
	Cl		Boil in $C_6H_5NO_2$	55	(219)
		160–180	Boil in $C_6H_5NO_2$	58	(229a)
			Boil in $C_6H_5CH_3$ or $C_6H_5NO_2$		(194)
	I	230	Sealed tube	63	(90, 92, 106, 215)
		207	Slow reaction		(132)
	I	205–240		35	(216)
		204	Slow reaction		(132)
	I	210–260		54	(114, 216, 225)
		260		60	(140)
		211.5	Slow reaction		(132)
	I	250–290			(137)
	I				(207)
	I	200		34	(95)

TABLE 1—*Continued*

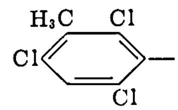
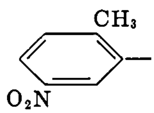
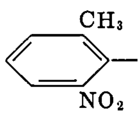
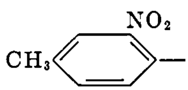
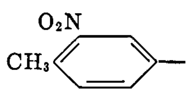
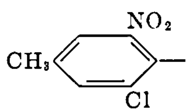
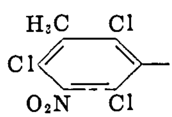
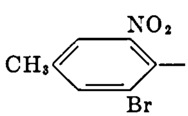
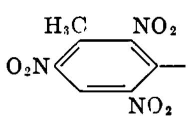
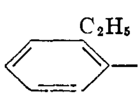
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	I	235–250			(237)
	I	220–270		22	(151)
				Poor	(37, 128, 132)
	I	180–235		80	(121, 240)
					(89, 99, 132, 139, 157, 233)
	Cl				(89, 221)
	Cl	260			(128)
	I		Boil in $C_6H_5NO_2$	39	(147)
		240–260			(48)
	Cl	240	Slow reaction		(132)
	I	230–250			(29)
	I	235–250			(236)
	I		In solution		(244)
	Br	160–183	In $C_6H_5NO_2$	70	(18)
	I	245–255			(131)
		226	Slow reaction		(132)

TABLE 1—*Continued*

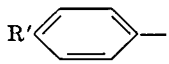
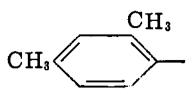
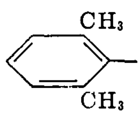
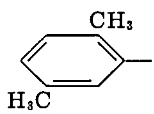
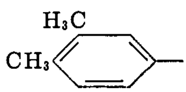
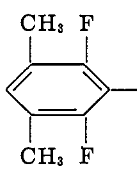
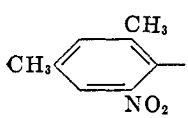
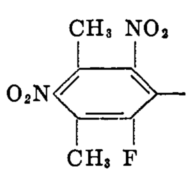
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
					
R′ = C_2H_5	I			50	(178)
R′ = $(CH_3)_2CH$	I				(178)
R′ = n-C_4H_9	I	300			(19)
R′ = $C_2H_5(CH_3)CH$	I	300			(19)
R′ = $(CH_3)_3C$	I				(178)
R′ = $C_2H_5(CH_3)_2C$	I	300		40	(19)
	I	230–260		86	(216)
		300	Sealed tube	60	(167)
		232	Slow reaction		(132)
	I	240–265		21	(33a)
	I	230–260		46	(216)
		229	Slow reaction		(132)
	I	220–268		23	(44)
	I	200		60	(95)
	I				(233)
	Br	200	In $C_6H_5NO_2$	75	(93)
	Br	190	In $C_6H_5NO_2$	69	(93)

TABLE 1—*Continued*

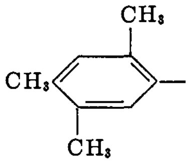
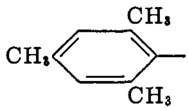
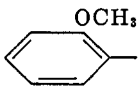
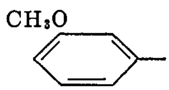
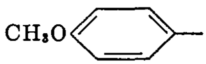
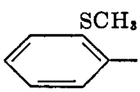
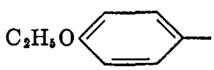
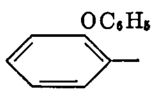
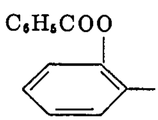
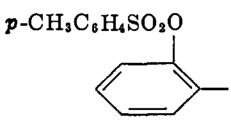
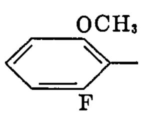
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	I	230–250		50	(216)
	I	260–270		Poor	(145, 216)
	I	210–260 213	 Rapid reaction	88	(216) (132) (225)
	I	240	Moderate reaction		(132) (225)
	I	230–240 225	 Moderate reaction	85	(216) (132)
	I	200–250		80	(24)
	I	230–240		75	(216)
	I	200–220			(111)
	I	215–260		40	(216)
	I	260			(216)
	I	180–200		65	(14)

TABLE 1—*Continued*

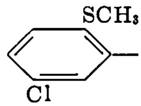
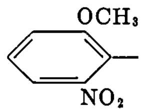
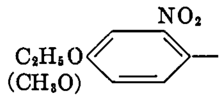
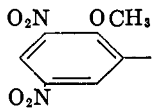
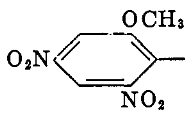
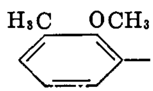
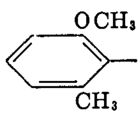
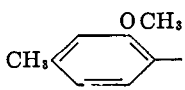
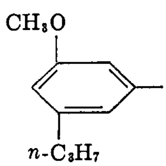
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	I	200–280		25	(23)
	Cl	180–210	In $C_6H_5NO_2$	70	(2)
	I	240 185–220 130–170			(225) (22) (71)
	I		Boil in $C_6H_5NO_2$	12	(37a)
	Cl		Boil in $C_6H_5NO_2$		(227)
	Cl	235		Poor	(226)
	I	240			(209)
	I				(209)
	I				(209)
	I	270			(208)

TABLE 1—*Continued*

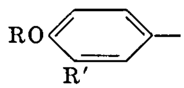
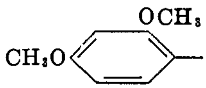
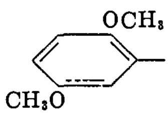
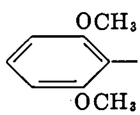
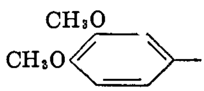
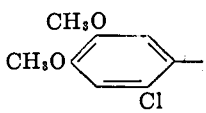
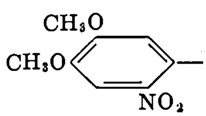
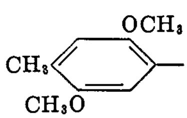
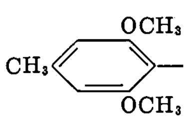
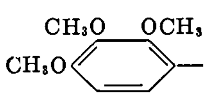
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	I		Cu not specified		(26)
	I	260	CO_2 atmosphere	75	(193)
	I	215–260		93	(216)
	I	170–210 170–190		85–90	(229) (185)
	I I	260–270 260	CO_2 atmosphere CO_2 atmosphere	90	(193) (181)
	I	270–280	CO_2 atmosphere	20	(181)
	Br	210–240		70	(74)
	I				(239a)
	I				(148a)
	I				(56)

TABLE 1—*Continued*

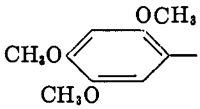
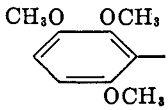
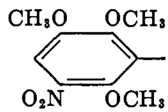
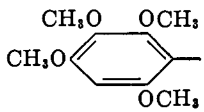
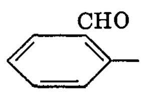
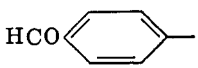
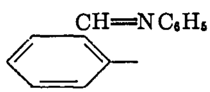
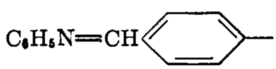
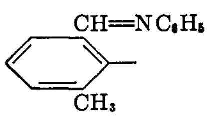
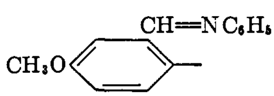
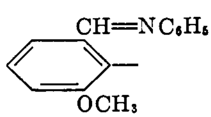
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	Br	250–270			(59)
	I	185–215	N_2 atmosphere	76	(63a)
	I	210–230		15	(63a)
	I	230			(55)
	I	200–220		70	(153)
		200–220	Isolated as the dioxime		(133)
	Cl	208	Slow reaction		(132)
	I		Isolated as the phenylhydrazone		(216)
	I	160–180	H_2 atmosphere	74	(134, 234)
	I	260			(216)
	I	160	H_2 atmosphere		(135)
		210	H_2 atmosphere		(134)
	I	160–180	H_2 atmosphere		(135)
	I	200	H_2 atmosphere		(134)

TABLE 1—*Continued*

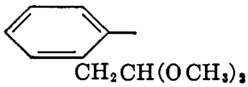
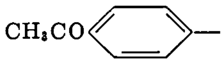
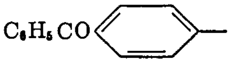
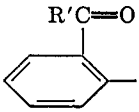
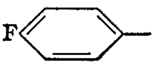
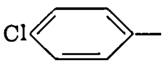
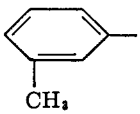
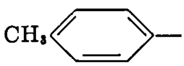
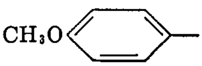
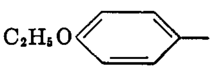
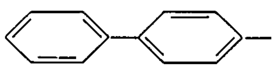
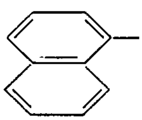
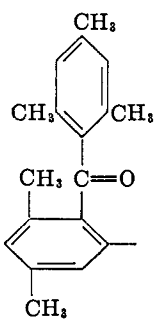
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	I	235–260		82	(234)
	I	235–260		25	(60)
	I	250		55	(216)
	Br				
R′ = 		200		30	(9)
R′ = 				0	(9)
R′ = 		250		38	(9)
R′ = 		200		68	(7)
R′ = 		200		50	(7)
R′ = 		250		57	(9)
R′ = 		200		22	(9)
R′ = 		200		66	(9)
	Br	200		65	(58)

TABLE 1—*Continued*

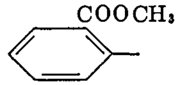
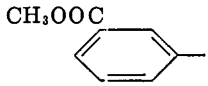
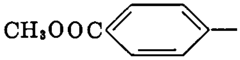
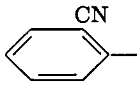
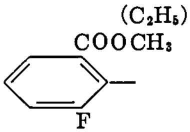
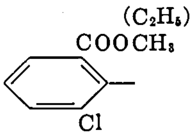
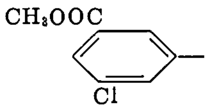
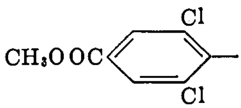
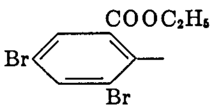
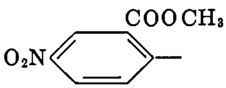
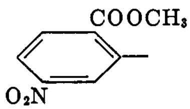
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	I	250–260		82	(216)
	I	260		60	(216)
	I	220–260		70	(211, 212, 216)
	I	275			(68)
	I	180–240		57	(196)
	I	180–240			(39)
	I	265–270		25	(137)
	I	280	Sealed tube		(146)
	I				(243)
	Br	180–220			(219)
	I	200		75	(149; *cf.* 37)

TABLE 1—*Continued*

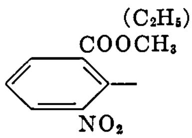
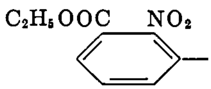
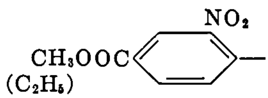
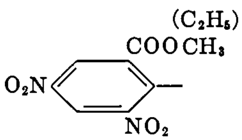
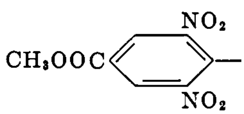
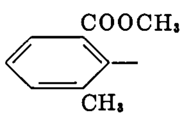
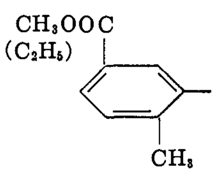
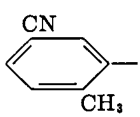
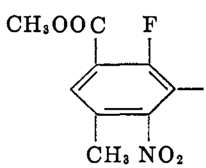
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	Cl Br or I	210–235 165–175		80–85 83	(89) (82, 89, 101)
	Br	180			(31)
	Br I	170–185	 Boil in $C_6H_5NO_2$	81 69	(219) (180)
	Cl	140–160		62	(39a, 102, 111, 217)
	Cl		Boil in $C_6H_5NO_2$	54	(219)
	I	220 270		Poor	(133) (15)
	I	260		55–65	(92)
	I	260		Poor	(92)
	Br	220–225		65	(94)

TABLE 1—*Continued*

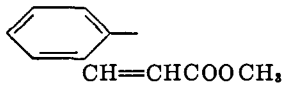
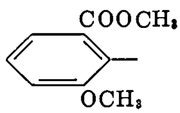
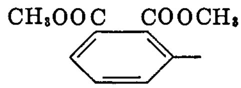
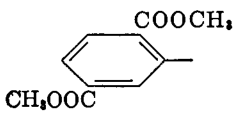
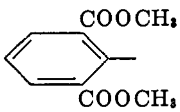
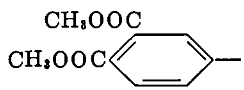
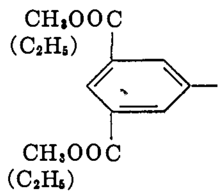
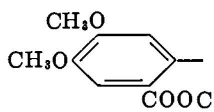
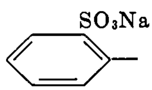
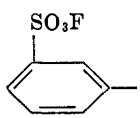
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	I	200–300		Poor	(234)
	I	205–215		70	(91, 196)
	I	240–260			(87, 88)
	I	260–310		70	(92)
	I	140–200			(133, 140)
	I	260			(88)
	I	220–250			(30)
	Br	255–260			(96)
	I		Boil in aqueous solution with $CuSO_4$	75	(13)
	I	200–230		54	(200)

TABLE 1—*Continued*

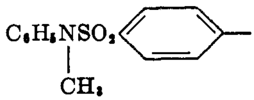
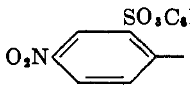
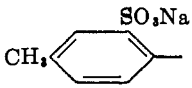
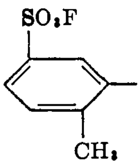
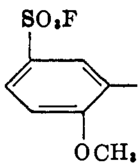
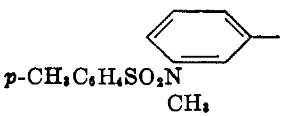
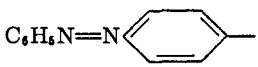
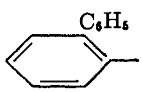
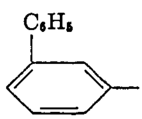
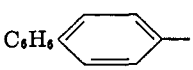
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	I	210–240			(216)
	I Cl	205 275		75 Poor	(112) (112)
	I		Boil in aqueous solution with $CuSO_4$		(13)
	I	220		41	(200)
	I	220			(200)
	I	212–230			(216)
	I	260			(216)
	I	255–310		72	(10, 21)
	I				(21)
	I Br	220–270 295–300		82.5 Trace	(21, 216; *cf.* 62) (21)

TABLE 1—*Continued*

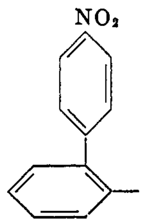
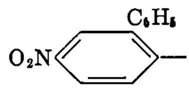
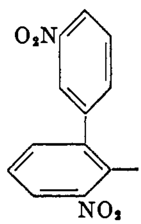
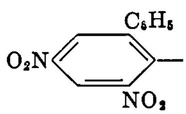
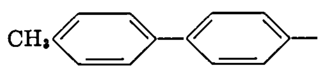
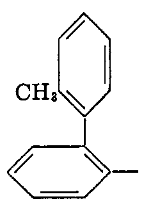
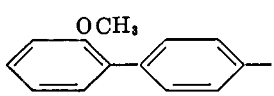
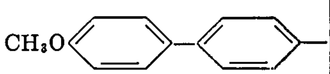
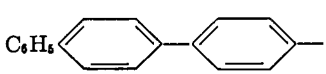
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	I				(158)
	I				(159)
	I	190–195			(160)
	Cl	215		Small	(21a)
	I	220		60–70	(152)
	I	265–285		70	(156)
	I	280	N_2 atmosphere	70	(70)
	I	280	N_2 atmosphere		(70)
	I	280–300		Poor	(150)

TABLE 1—*Continued*

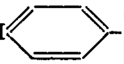
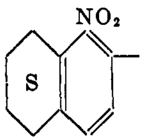
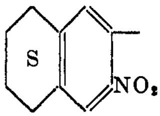
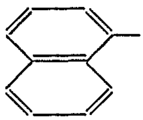
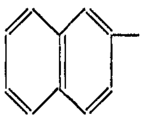
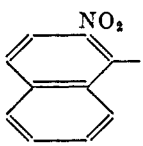
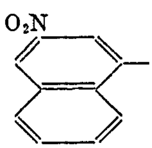
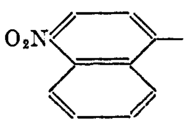
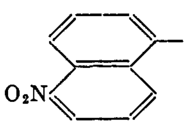
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
$[p\text{-}(CH_3)_2NC_6H_4]_2CH$	Br	210–220	H_2 atmosphere		(50)
	I	135–190		20	(45)
	I	110–140		80	(45)
	I Br	260–285 280–285	 I_2 added	74–92 50	(25, 219) (177)
	I	230–260		67.5	(216)
	I	120–130		70	(40, 45)
	I			20	(40, 45)
	I	220–230	In naphthalene	50	(40, 177)
	I	220–230		60	(174)

TABLE 1—*Continued*

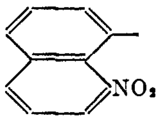
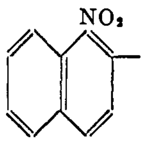
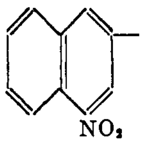
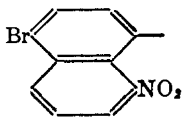
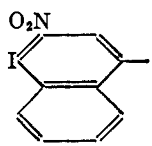
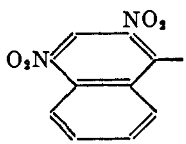
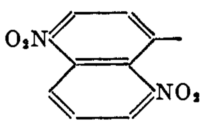
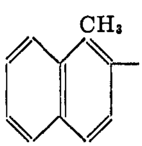
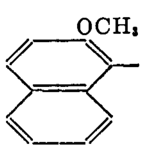
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	I		Boil in $C_6H_5NO_2$	43	(73)
	I		Boil in $C_6H_5NO_2$	50	(40, 231)
	I		Boil in $C_6H_5NO_2$	30	(72)
	I		Boil in $C_6H_5NO_2$	29	(73)
	I		In $C_6H_5NO_2$		(72)
	Cl		Boil in $C_6H_5NO_2$		(40, 154)
	I		Boil in $C_6H_5NO_2$	36	(73)
	I	220–260			(175; *cf.* 235)
	I	200–210	I_2 added	30	(41)

TABLE 1—*Continued*

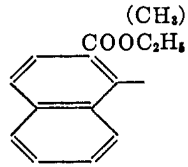
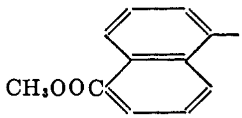
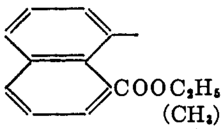
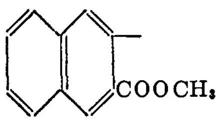
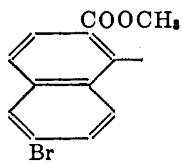
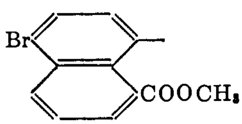
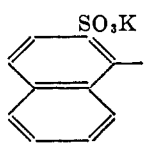
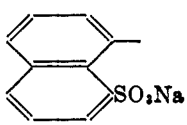
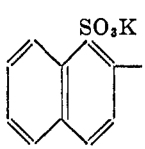
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	Br Cl	190 300		60	(124) (86)
	I	220–240	CO_2 atmosphere	75	(182)
	Cl	290–300	I_2 added		(85, 86, 104)
	Br	190–200		90	(124)
	Br	160–170		41	(155a)
	Br	210–220		55	(155a)
	I		Boil in aqueous solution with $CuSO_4$		(13)
	I		In aqueous solution with $CuSO_4$		(46)
	I or Br		In aqueous solution with $CuSO_4$		(46)

TABLE 1—*Continued*

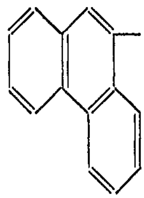
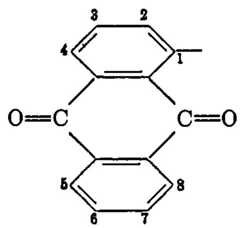
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	Br	330–350		10	(246; *cf.* 8)
	Cl		Boil in $C_6H_5NO_2$	70–80	(142, 224)
	I	210–275	CO_2 atmosphere	20	(168)
	—SCN or —SS—	220–240	In anthracene		(97)
	X				(12)
Substituted 1,1'-bianthraquinolyls:					
3-Cl	Cl		Boil in $C_6H_5NO_2$		(53)
4-Cl	Cl		Boil in $C_6H_5NO_2$		(53)
2-Br	Br	200–210	In $C_6H_5NO_2$	68	(179)
3-Br	Br		Boil in $C_6H_5NO_2$	65	(220)
2-NO_2	Cl		In $C_6H_5NO_2$		(98)
2-substituted	X				(187, 188)
2-CH_3	I	210–290		30–50	(103, 162)
	Cl	225–230	Boil in $C_{10}H_8$		(165)
	—SS—				(97)
	X				(11)
3-CH_3	Br		Boil in $C_6H_5NO_2$	50–70	(155)
4-CH_3	Cl		Boil in $C_6H_5NO_2$	70	(224)
2-C_2H_5	I	240	CO_2 atmosphere	50	(173)
2-*n*-C_3H_7	I	200	CO_2 atmosphere		(173)
2-$(CH_3)_2CH$	I	200	CO_2 atmosphere	75	(173)
2-CH_3, 4-CH_3	I	210–250	CO_2 atmosphere	35	(163)
2-OH	—SCN or —SS—				(97)
2-OCH_3	I	360		20	(17)
4-OCH_3	Br or Cl		Boil in $C_6H_5NO_2$		(52)

TABLE 1—*Continued*

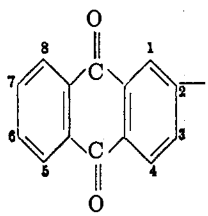
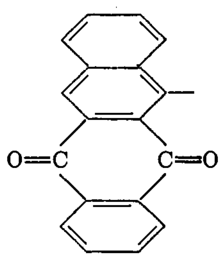
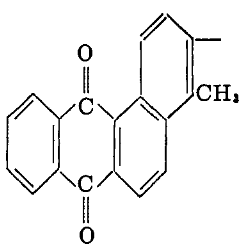
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
2-C_6H_5COO	Br		Boil in $C_{10}H_8$		(69)
3-OCH_3, 4-OCH_3	I	310	CO_2 atmosphere	53	(181)
2-CHO	Cl				(12a, 83)
2-CHO, 6- or 7-Cl	Cl		In a solvent		(12a)
2-$COOC_2H_5$	Cl		Boil in $C_6H_5NO_2$	75	(169)
4-$COOCH_3$	Cl	250–300		40	(195)
4-C_6H_5COO, 3-CH_3O	Br		Boil in $C_6H_5NO_2$ or $C_{10}H_8$		(148)
2-$NCHC_6H_5$	Cl	220–240			(166)
2-$NCHC_6H_5$, 3-Br	Br	220–260	In $C_{10}H_8$	51	(218, 223)
2-$NHCOOC_2H_5$	Cl	135–175			(189)
2-$N(COR)_2$	X				(77, 78, 80, 81)
	I	230–330	CO_2 atmosphere	30	(171)
Substituted 2,2'-bianthraquinolyls:	I	360		2	(17)
1-OCH_3	I		Boil in $C_{10}H_8$		(69)
1-C_6H_5COO	Br		Boil in $C_6H_5NO_2$	58	(170)
1-CN					
	Cl	220–230	In $C_6H_5NO_2$		(232; *cf.* 76)
	I	200–360	CO_2 atmosphere		(172)

TABLE 1—*Continued*

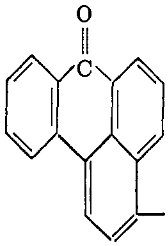
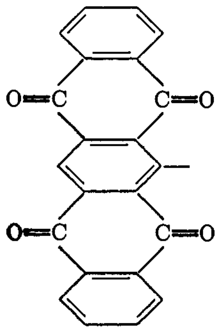
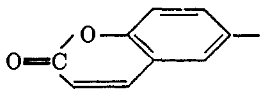
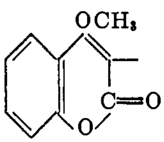
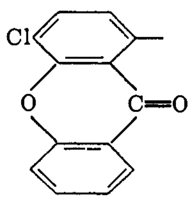
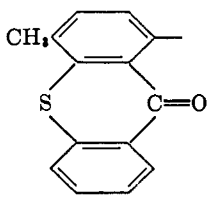
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	Br	280–300			(122)
	Br or Cl		Boil in $C_6H_5NO_2$		(47)
	I				(183)
	Br	210		30	(73a)
	Cl		Boil in $C_{10}H_8$		(51)
	Cl		Boil in $C_{10}H_8$	46	(222)

TABLE 1—*Continued*

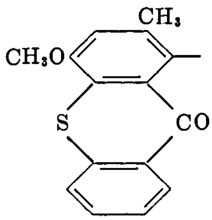
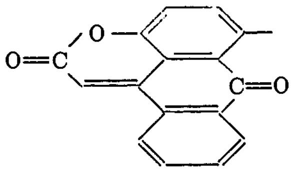
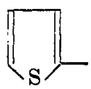
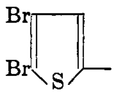
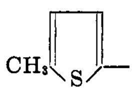
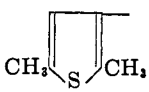
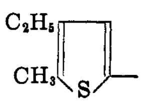
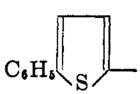
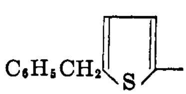
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		*per cent*	
	Cl		Boil in $C_{10}H_8$	57	(222)
	Cl		Boil in $C_6H_5NO_2$	40	(143)
	I	190–210			(201)
	I	240			(197a)
	I	150–220		75–81	(202)
	I	220–250		47	(198, 204)
	I	210–245		20	(203)
	I				(201)
	I	185–210		14	(199)

TABLE 1—*Concluded*

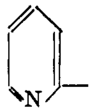
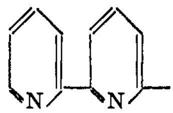
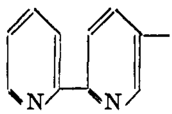
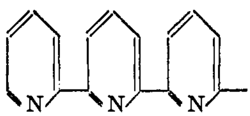
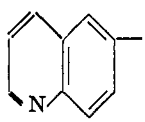
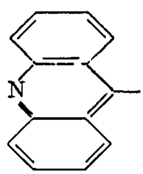
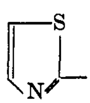
R	X	TEMPERATURE	REMARKS	YIELD	REFERENCE
		°C.		per cent	
	I	180	In *p*-cymene	20	(238)
	Br	180	In *p*-cymene	60	(238)
		230	In $C_6H_5C_6H_5$	70	(28)
	Br		Boil in $C_6H_5C_6H_5$	30	(28)
	Br		Boil in $C_6H_5C_6H_5$		(28)
	Br			30	(28)
	I	220–340	Violent reaction		(216)
	Cl	140	In absence of air	60	(108)
	Br	170–180	In *p*-cymene		(57)

TABLE 2

Unsymmetrical biaryls prepared by the reaction $RX + R'X' \xrightarrow{Cu} RR'$

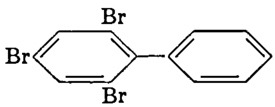
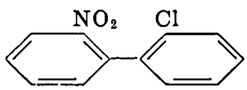
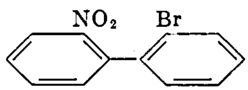
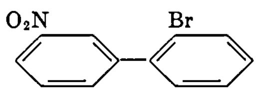
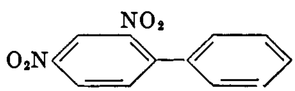
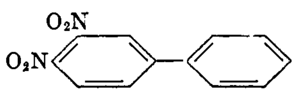
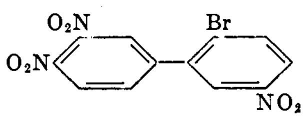
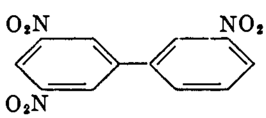
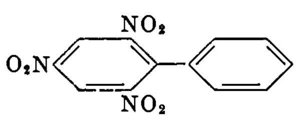
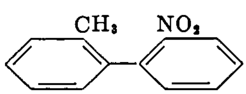
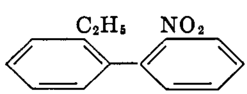
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		per cent	
	I	I	200		40	(35)
	I	I	200–225		25	(127)
	I or Br	I				(126, 127)
	I	I	250		10	(34)
	Cl	I	210–230		20	(66)
	I	I	280	Sealed tube	15	(36)
	I	I				(36b)
	I	I	270		Poor	(36)
	Cl	I	160–165		85	(66, 155a)
	I	I	220–260		25–37	(156, 184a)
	I	Cl	260–270			(131)

TABLE 2—*Continued*

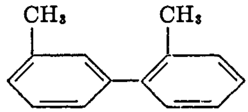
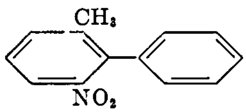
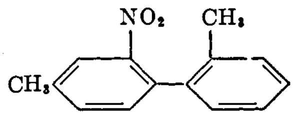
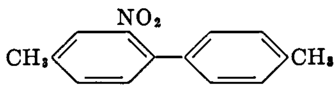
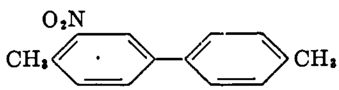
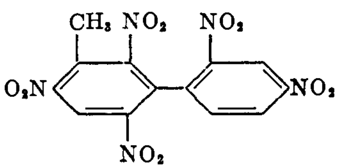
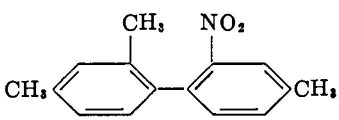
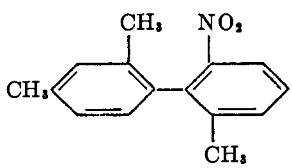
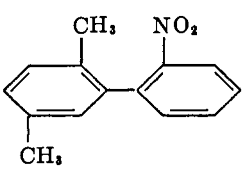
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		*per cent*	
	I	I	230–240	In a bomb		(136)
	Br	I	175–230		30	(156)
	I	I	260			(128)
	Br	I	225–260			(123)
	I	I	230–250			(123)
	Br	Cl	160–165	In $C_6H_5NO_2$	40	(197)
	X	X				(116)
	I	I	240–250			(131)
	I	I	230–260			(129)

TABLE 2—*Continued*

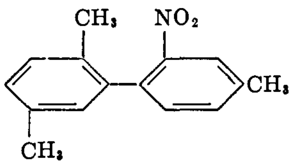
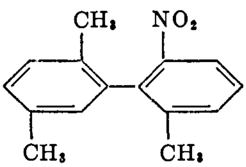
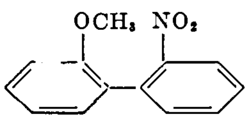
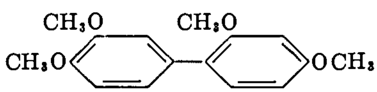
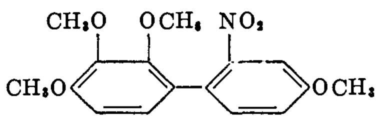
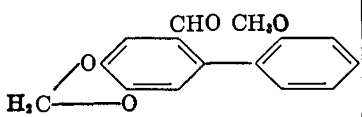
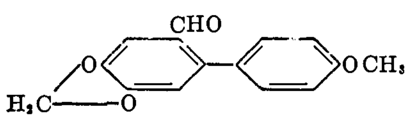
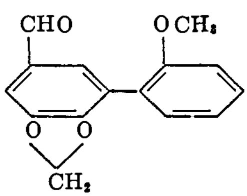
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		*per cent*	
	I	I				(117)
	X	X				(118)
	I	I				(125)
	I	I	260	CO_2 atmosphere	15	(193)
	I	Br	230–245		30	(210a)
	Br	I			20	(214)
	Br	I			20	(217)
	Br	I	220–230		15	(214)

TABLE 2—*Continued*

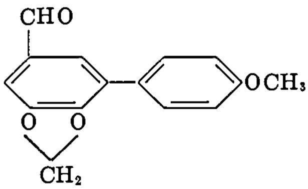
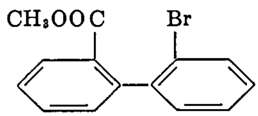
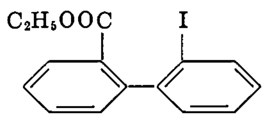
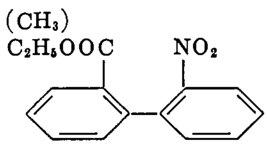
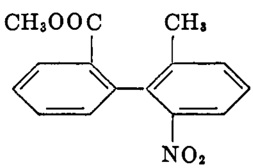
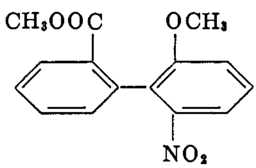
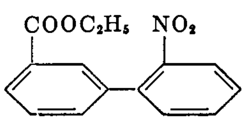
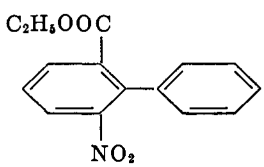
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		*per cent*	
	Br	I	220–250		5	(214)
	I	I	260–290		14	(141)
	I	I	280–300		35	(184a)
	I	I	230–270			(15)
	Br	I	250–285		20–68	(156, 184a)
	I	Br	270–300		27	(206)
	I	Cl	255–280		5	(2)
	I	Br	215–250		31	(1)
	Br	I	200–250			(156)

TABLE 2—*Continued*

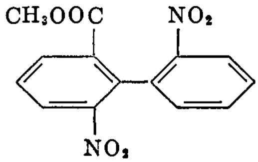
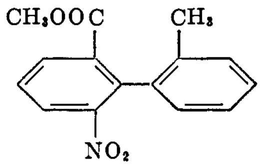
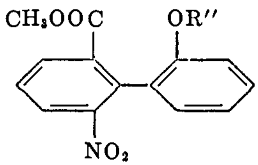
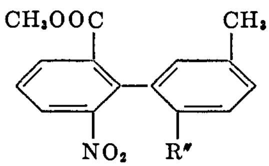
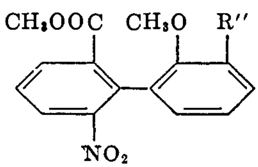
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		*per cent*	
	Br	I	220–225		30	(4)
	Br	I	225–230		15	(4)
						
R″ = CH_3	Br	I	240–250		18.4	(113, 207)
R″ = C_2H_5	Br	I	240–250		16.5	(113)
R″ = n-C_3H_7	Br	I	250–260		5.7	(113)
R″ = n-C_4H_9	Br	I	210–220		10.6	(113)
R″ = n-C_5H_{11}	Br	I	220–230		11.0	(113)
						
R″ = F	Br	I			16	(207)
R″ = Cl	Br	I			11	(207)
R″ = Br	Br	I			10	(207)
						
R″ = Cl	Br	I	220–250		7.9	(38)
R″ = Br	Br	I	220–250		3.7	(38)
R″ = NO_2	Br	I	220–250		15.5	(38)
R″ = CH_3	Br	I	240–280		18.7	(38)
R″ = OCH_3	Br	I	220–250		17.2	(38)

TABLE 2—*Continued*

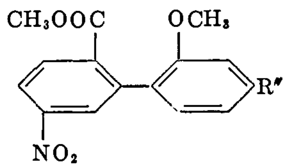
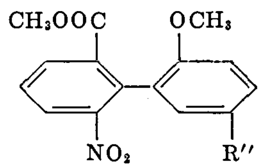
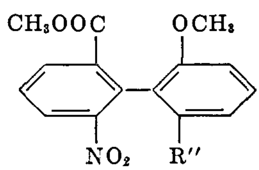
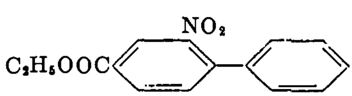
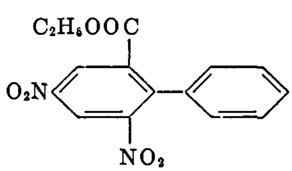
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		per cent	
						
R″ = Cl	Br	I	205–215		10	(67)
R″ = Br	Br	I	240–250		10	(67)
R″ = NO_2	Br	I	230–240		10	(67)
R″ = CH_3	Br	I	205–215		10	(67)
R″ = OCH_3	Br	I	240–290		10	(67)
						
R″ = Cl	Br	I	240		30	(242)
R″ = Br	Br	I	200–215		30	(242)
R″ = NO_2	Br	I	230–240		10	(242)
R″ = CH_3	Br	I	240–260		15	(242)
R″ = OCH_3	Br	I	260–300		30	(241)
						
R″ = F	Br	I	210–240		1	(228)
R″ = OCH_3	I	I	240–300		12	(228)
	Br	I	235–245			(65)
	I	Cl	240		70	(109)

TABLE 2—*Continued*

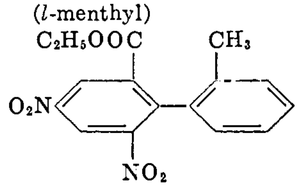
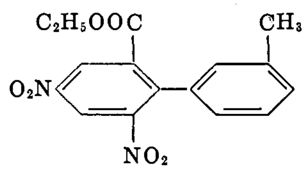
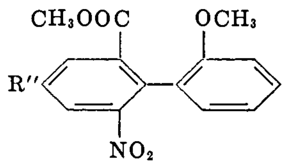
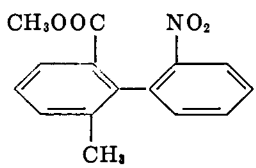
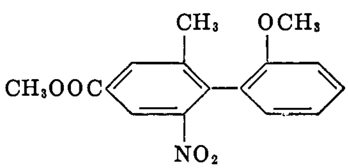
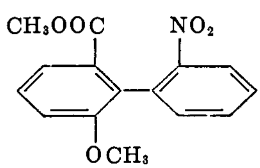
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		*per cent*	
(*l*-menthyl) 	Cl	I	220		50	(109)
	Cl	I	230		90	(109)
						
R″ = Cl	I	I	210–230		45	(5)
R″ = Br	I	I	210–230		27	(5)
R″ = NO_2	I	I	215	In $C_6H_5NO_2$	23	(5)
R″ = CH_3	I	I	215	In $C_6H_5NO_2$	5	(5)
	I	I	230–250		50	(4)
	Br	I	240–270		28	(6, 213)
	I	I	200			(2)

TABLE 2—*Continued*

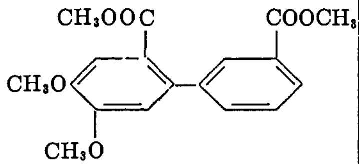
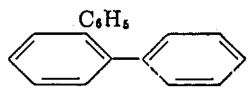
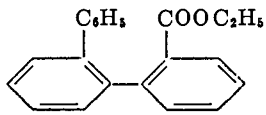
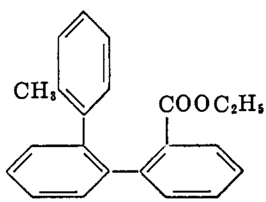
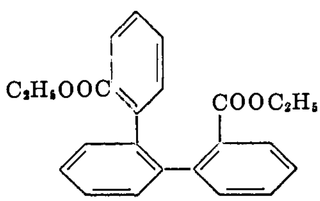
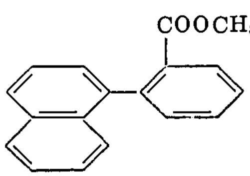
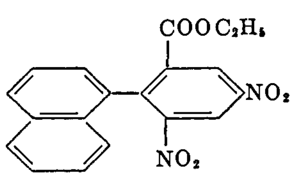
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		per cent	
	Br	I	255–260		60	(96)
	I	I	240	Sealed tube	50	(10)
	I	Br	275			(156)
	I	Br	255–290		2	(156)
	I	I	280–320		5	(184a)
	I	I	280		30	(10d)
	I	Cl	210		70	(110)

TABLE 2—*Continued*

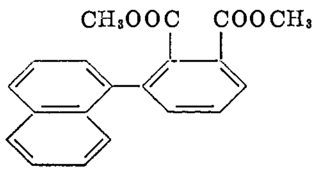
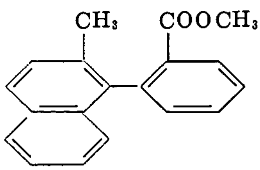
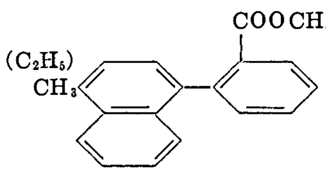
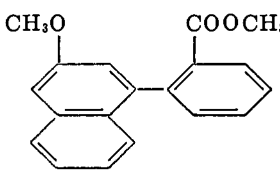
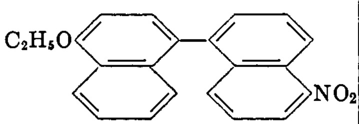
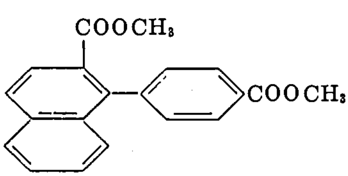
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°*C.*		*per cent*	
	I	I		Boiling $C_6H_5NO_2$ bath	36	(10b)
	I	Br	255–260		10	(6a)
	I	I	180–190			(10c)
	I	I	180–190		10	(10a, 10d)
	I	I	180–210		26	(10b)
	I	I	220	CO_2 atmosphere		(210)
	Br	I	200–265		20	(10b)

TABLE 2—*Continued*

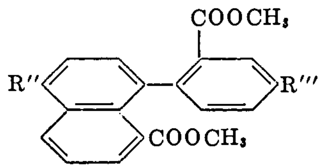
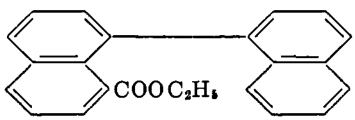
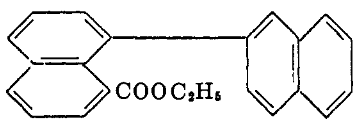
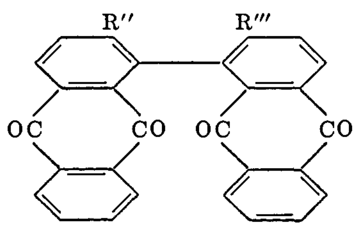
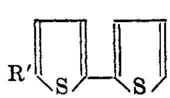
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		*per cent*	
						
R″ = H; R‴ = H	Br	Br or I	180–195		41–75	(155a, 155b)
R″ = H; R‴ = Br	Br	I	180		60	(155a)
R″ = H; R‴ = NO_2	Br	Br or I	180		33–41	(155a)
R″ = Br; R‴ = H	Br	I	180		49	(155a)
R″ = Br; R‴ = Br	Br	I	180		49	(155a)
R″ = NO_2; R‴ = H	Br	I	180		49	(155a)
	Cl	Br	290		10	(138)
	Cl	Br	290		10	(138)
						
R″ = CH_3CONH; R‴ = H	X	X				(144, 190)
R″ = C_6H_5CHN; R‴ = CH_3	Cl	Cl	225–230	In $C_{10}H_8$	10	(165)
R″ = $C_6H_4(CO)_2N$; R‴ = CH_3	Cl	Cl		Boil in $C_{10}H_8$		(79)
						
R′ = CH_3	I	I	180–200		40	(201)
R′ = C_6H_5	I	I	190–218		Poor	(201)

TABLE 2—*Concluded*

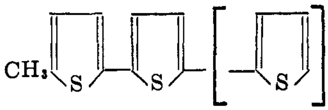
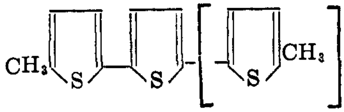
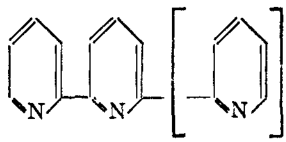
RR′	X	X′	TEMPERATURE	REMARKS	YIELD	REFERENCE
			°C.		per cent	
	I	I	200			(201)
	I	I	200			(201)
	Br	Br		In $C_6H_5C_6H_5$	5	(28)

TABLE 3

Unsuccessful reactions

A. Attempted syntheses of symmetrical biaryls

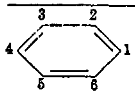
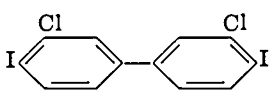
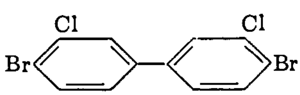
REACTANT	REFERENCE
	
Derivatives of benzene:	
1-Cl, 3,4-di-NO_2	(216)
1-Cl, 2-Cl, 4,6-di-NO_2	(227)
1-Cl, 2-NO_2, 3-CH_3	(64)
1-I, 4-$C(CH_3)_2C_2H_5$	(178)
1-I, 3-Br, 5-CH_3	(137)
1-I, 2,4,6-tri-CH_3, 3-NO_3	(145)
1-I, "phenols"	(216)
1-I, 3-OH, 6-CH_3	(151)
1-I, 3-$OCOC_6H_5$, 6-CH_3	(151)
1-Cl, 2,4,6-tri-NO_2, 3-OCH_3	(176)
1-Br, 2-F, 3,5-di-CH_3, 6-OCH_3	(14)
1-Cl, 2,4,6-tri-NO_2, 3,5-di-OCH_3	(176)
1-I, 2-$CH(OC_2H_5)_2$	(153)
1-I, 2-$CH{=}CHCOOCH_3$	(133)
1-I, 3-Br, 5-$COOCH_3$	(137)
1-I, 3-NO_2, 5-$COOC_2H_5$	(137)
1-Br, 2-NO_2, 4-$N(CH_3)_2$	(16)
1-I, 4-SO_3H	(216)
1-I, 4-$SO_3Ca_{1/2}$	(216)
1-I, 4-SO_3NH_2	(216)
1-I, 4-$SO_2NHC_6H_5$	(216)
1-I, 3 or 4-NH_2	(216)
1-I, 4-$NHCOCH_3$	(216)
1-I, 4-$NHCH_3$	(216)
	(33)
	(33)

TABLE 3—*Continued*

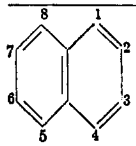
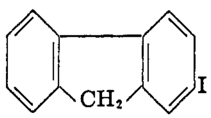
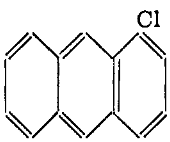
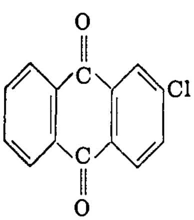
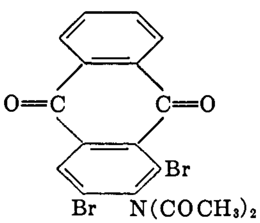
REACTANT	REFERENCE
	
Derivatives of naphthalene:	
2-I, 3-NO_2	(72)
1-I, 2,4-di-Br, 8-NO_2	(73)
1-Cl, 2,4,5-tri-NO_2	(154)
2-I, 3-CH_3, 6,7-di-OCH_3	(3)
2-Br, 3-CH_3, 1,4-di-$OCOCH_3$	(3)
2-Br, 3-CH_3, 1,4-di-OCH_3	(3)
1-Br, 2-SO_3Na	(46)
1-Cl, 4-SO_3Na	(46)
1-I, 5-SO_3Na	(46)
2-I, 6-SO_3Na	(46)
1-I, 2-SO_3Na	(46)
1-I, 4-SO_3Na	(46)
Penta- and hexabromo derivatives of 2,7,2′,7′-tetrahydroxy-1,1′-binaphthyl	(75)
	(100)
	(164)
	(224)
	(162)

TABLE 3—*Continued*

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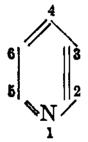
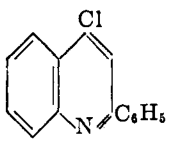
	
Derivatives of pyridine:	
2-Cl	(238)
2,5-di-Br	(239)
2,6-di-Br	(239)
2,3,5-tri-Br	(239)
2-Br, 6-CH_3	(239)
2-Br, 6-OC_2H_5	(239)
2-Br, 6-NH_2	(239)
	(84)

B. Attempted syntheses of unsymmetrical biaryls

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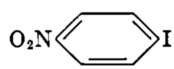
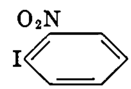
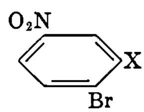
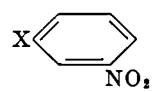
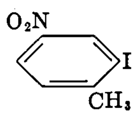
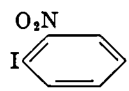
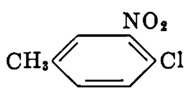
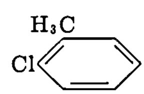
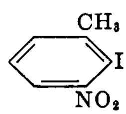
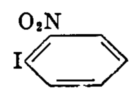
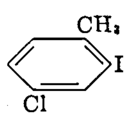
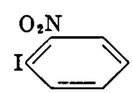
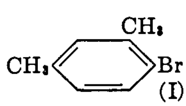
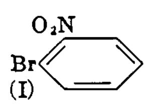
		(60a)
		(36b)
		(119)
		(128)
		(128)
		(128)
		(128)

TABLE 3—*Continued*

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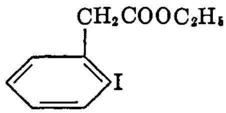
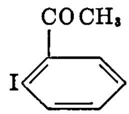
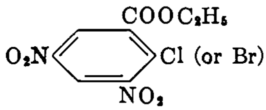
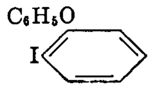
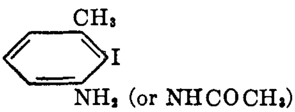
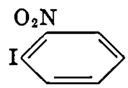
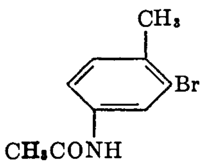
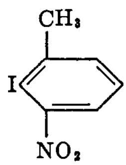
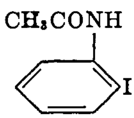
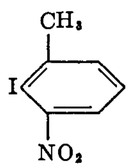
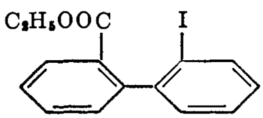
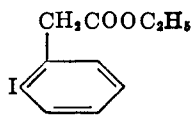
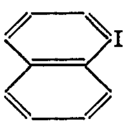
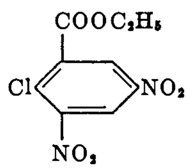
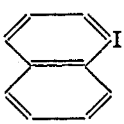
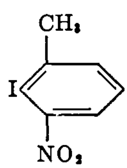
		(153)
		(111)
		(15)
		(15)
		(15)
		(184a)
		(111)
		(15)

TABLE 3—*Concluded*

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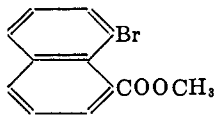
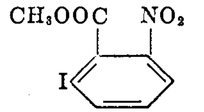
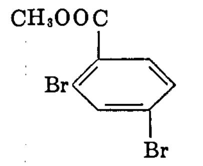
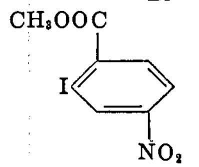
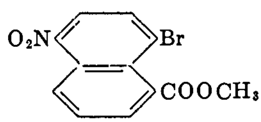
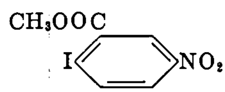
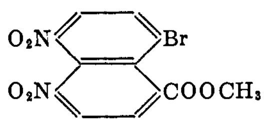
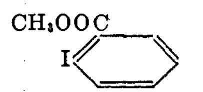
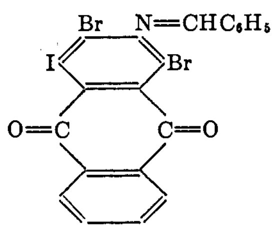
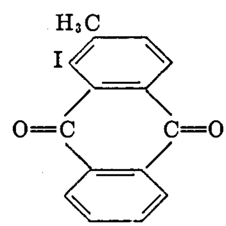
		(155a)
		(155a)
		(155a)
		(155a)
		(155a)
		(165)

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