

ALKYLATION AND ARYLATION: THE EXPECTED AND UNEXPECTED

J. I. G. CADOGAN

University of St. Andrews, St. Andrews, Scotland

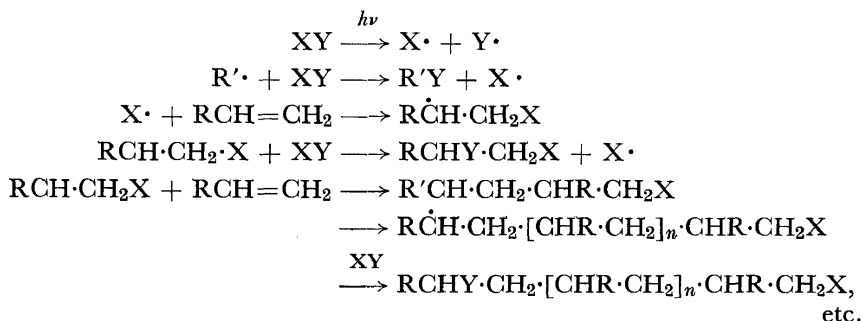
INTRODUCTION

Alkylation and arylation are classic reactions in radical chemistry and some of the great names in this field are associated with these processes. Such names include Gomberg himself, who laid the foundation of homolytic substitution of aromatic systems; Hey and Waters, who were subjected to and overcame much criticism in the 'thirties and early 'forties for their theories of free radical reactions; and Kharasch, whose work on homolytically induced addition reactions of olefinic systems was a major growth point in radical chemistry.

It was with these names, and the chemistry associated with them, in mind that the title of this lecture was chosen. The purpose of my talk is to describe some of our more recent investigations in the fields of alkylation and arylation and thereby to show that these areas, which have been so thoroughly investigated since the early days, are still providing surprises.

ALKYLATION

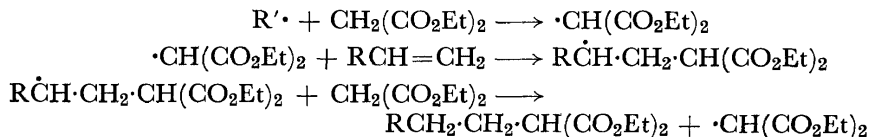
Work on alkylation was inspired by the Kharasch reaction: radical-induced addition to double bonds, exemplified in a general way as follows:



The variables in this reaction include the ease of homolysis of the bond $X-Y$, and the reactivity, which depends on the structure of the olefins, of the various intermediate radicals towards the many different species present.

When Y is hydrogen this reaction becomes a simple alkylation and by suitable manipulation of the reaction conditions, e.g. concentration, temperature, and radical initiator we have been able to realize many of the synthetic possibilities inherent in this reaction. Thus, using a high dilution

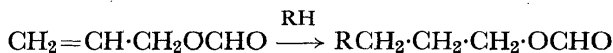
technique¹, whereby a solution of the olefin and a small amount of a radical initiator (di-*t*-butyl or benzoyl peroxide) in diethyl malonate is added dropwise to hot diethyl malonate, side reactions such as telomerization, and chain termination processes are suppressed leading to good yields (80 per cent) of the 1:1 adduct, the diethyl alkylmalonate.



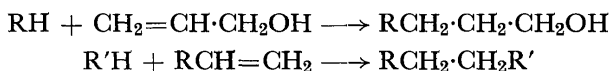
Similar alkylations of other compounds containing activated methylene or activated methine groups also proceed quite readily and in many cases are easier to effect than the corresponding classical ionic reactions involving alkyl halides and sodium salts (*Table 1*).

The presence of an activated methylene group is not essential for successful addition as is shown by the results of experiments carried out with derivatives of acetic acid (*Table 2*), although in these cases, high dilution was necessary to suppress side reactions sufficiently to give good yields of alkylated products.

By the use of suitable dilutions the addition reaction may be effected with addenda containing no functional groups at all. Thus an attempt to induce radical cyclization of allyl formate by reaction with benzoyl peroxide in cyclohexane led to the addition of cyclohexane to the double bond,

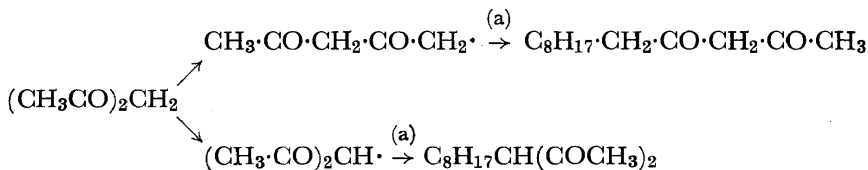


and it is clear that this reaction is capable of many extensions, *e.g.*⁴



Ramifications of these reactions⁵ investigated by us include cyclizations similar to those described by Julia and coworkers⁶.

A significant feature of many of the reactions summarized in *Tables 1 and 2* is that radical alkylation of the addendum takes place at more than one position corresponding to chain transfer to give several possible radicals. In the case of acetylacetone two points of attack, C₁ and C₃, are possible,



(a) = addition to oct-1-ene followed by chain transfer

and products corresponding to addition of both of these radicals to the olefin were detected. The relatively high proportion of product corresponding to attack at the C₁ position was at first sight unexpected since it might

Table 1. Typical examples of addition of compounds containing activated methylene or methine groups to oct-1-ene²

Addendum	1:1 Adducts (%)		A/B
	A	B	
Et·CH(CO ₂ Et) ₂	<i>n</i> -C ₈ H ₁₇ ·C(CO ₂ Et) ₂ ·Et (54·4)	<i>n</i> -C ₈ H ₁₇ ·CH(CO ₂ Et) ₂ ·CH(CO ₂ Et) ₂ (7·6)	7·2
<i>n</i> -Bu·CH(CO ₂ Et) ₂	<i>n</i> -C ₈ H ₁₇ ·C(CO ₂ Et) ₂ · <i>n</i> -Bu (31·8)	<i>n</i> -C ₈ H ₁₇ ·CH(CO ₂ Et) ₂ ·CH(CO ₂ Et) ₂ (4·2)	7·5
CH ₂ (CO ₂ Pr) ₂	<i>n</i> -C ₈ H ₁₇ ·CH(CO ₂ Pr) ₂ (55)	<i>n</i> -C ₈ H ₁₇ ·CH(CO ₂ Et) ₂ ·CH(CO ₂ Et) ₂ (17)	3·3
CH ₂ (CO ₂ Et) ₂ ·CH(CO ₂ Et) ₂	<i>n</i> -C ₈ H ₁₇ ·C(CO ₂ Et) ₂ ·CH ₂ ·CO ₂ Et (56)	<i>n</i> -C ₈ H ₁₇ ·CH ₂ ·CO·CH ₃ ·CO·CH ₃ (27·7)	1·5†
CH(CO ₂ Et) ₃	<i>n</i> -C ₈ H ₁₇ ·C(CO ₂ Et) ₃ (54)	<i>n</i> -C ₈ H ₁₇ ·CH ₂ ·CO·CH ₂ ·CO ₂ Et†	15·5
CH ₃ ·CO·CH ₂ ·CO·CH ₃	<i>n</i> -C ₈ H ₁₇ ·CH(CO·CH ₃) ₂ ·CO ₂ Et† (41·5)	<i>n</i> -C ₈ H ₁₇ ·C(CO·CH ₃) ₂ ·CO ₂ Et (8·2)	2·3
CH ₃ ·CO·CH ₂ ·CO ₂ Et	<i>n</i> -C ₈ H ₁₇ ·C(CO ₂ Et) ₂ ·CO·CH ₃ (32)		
CH ₃ ·CO·CH(CO ₂ Et) ₂	<i>n</i> -C ₈ H ₁₇ ·CH ₂ ·CO·CH(CO ₂ Et) ₂ ·CO ₂ Et (18·8)		
(CH ₃ ·CO) ₂ ·CH·CO ₂ Et	<i>n</i> -C ₈ H ₁₇ ·C(CO ₂ Et) ₂ ·CN (31)		
NC·CH(CO ₂ Et) ₂	<i>n</i> -C ₈ H ₁₇ ·C(CO ₂ Et) ₂ ·CO ₂ Et (35)		
PhCH ₂ ·CO ₂ Et	<i>n</i> -C ₈ H ₁₇ ·CHPh·CO ₂ Et (67)		
NC·CH ₂ ·CO ₂ Et	<i>n</i> -C ₈ H ₁₇ ·CH(CN)·CO ₂ Et (67)		

† This value varies with addendum to olefin ratio and with temperature.

 ‡ Yields of 1:1 adduct of up to 61 per cent have been reported.¹

Table 2. Typical radical-induced additions to oct-1-ene (1 mole):
 $\text{CH}_3\text{X} + \text{R}\cdot\text{CH}\cdot\text{CH}_2 \rightarrow \text{R}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{X}$

CH_3X (mole)	Initiator (mole) [†]	Temperature (°C)	$\text{R}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{X}$ (%) [‡]
MeCO_2H (300)	DTBP (0.15)	105	69
$(\text{MeCO})_2\text{O}$ (300)	DTBP (0.15)	140	73
$(\text{MeCO})_2\text{O}$ (50)	DTBP (0.15)	140§	72
$\text{MeCO}\cdot\text{Cl}$ (20)	PK (0.24)	107§	43
MeCN (10)	PK (0.47)	82§	18
$\text{CH}_2\cdot\text{Cl}\cdot\text{CO}_2\text{Et}$ (11)	DTBP (0.10)	155§	73
MeCO_2Me (100)	PK (0.24)	57§	9¶
$\text{MeCO}_2\cdot\text{C}_6\text{H}_{11}$ (50)	DTBP (0.10)	145	59
Me_2CO (22)	PK (0.24)	56§	32
$\text{MeCO}\cdot\text{Et}$ (100)	BP (0.05)	80	34¶
$\text{PhCO}\cdot\text{Me}$ (22)	DTBP (0.15)	155§	10
$\text{MeCO}\cdot\text{NH}_2$ (20)	DTBP (0.10)	155§	29
$\text{MeCO}\cdot\text{NHMe}$ (42)	DTBP (0.10)	155§	35¶
$\text{MeCO}\cdot\text{S}\cdot\text{Et}$ (22)	DTBP (0.10)	155§	10¶

[†] PK = Perkadox (di-isopropyl peroxydicarbonate). DTBP = Di-*t*-butyl peroxide. BP = Benzoyl peroxide.

[‡] Based on olefin added.

[§] Dropwise addition.

[¶] Isomeric mixture.

be thought that the C_3 radical would be much more easily formed and, being more electrophilic might be more reactive than the C_1 radical towards the electron rich olefin. On the other hand, delocalization of the free electron would be more likely in the C_3 radical. It was also of interest that the ratio of products corresponding to attack by C_1 and C_3 radicals varied with the ratio of olefin to acetylacetone, C_3 attack increasing relative to attack at C_1 with increasing ratio of acetylacetone to oct-1-ene and with increase in temperature. This unusual phenomenon can be related to the unusually high degree of enolization of acetylacetone (61 per cent at 105°). It has been shown by Kuratari⁷ that the degree of enolization of acetylacetone is increased by dilution with non-polar solvents, and this has been confirmed by us by a proton magnetic resonance study of various mixtures of oct-1-ene and acetylacetone. It is predictable, therefore, if the observed ratio of products, representing a high proportion of attack at C_1 , produced by the addition of acetylacetone to oct-1-ene is dependent on the extent of enolization, that this ratio of C_3 to C_1 attack will increase as the proportion of oct-1-ene in the reaction mixture is decreased, i.e. as the degree of enolization is decreased. This prediction is supported by experiment. P.m.r. studies have also shown that the degree of enolization of acetylacetone is decreased with rise in temperature hence it is predictable that for a given molar ratio of acetylacetone to oct-1-ene the ratio ($\text{C}_3:\text{C}_1$) will be higher at higher temperatures. This is also supported by the experimental results. These conclusions, drawn from experiments carried out with different ratios of reactants, are based on the acceptable assumption that the change in product ratio is not a function of preferential removal of one or other of the chain carrying radicals by telomer formation, which is more important at low concentrations of addendum. That is, it is assumed that the radicals $\text{C}_6\text{H}_{13}\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{COCH}_3)_2$ and $\text{C}_6\text{H}_{13}\dot{\text{C}}\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COCH}_3$

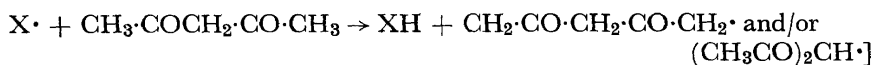
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have the same reactivity towards the double bond in oct-1-ene, which is reasonable since the radical centre is insulated by two carbon atoms from the only possible groups which might affect its reactivity. This conclusion is supported by the observation that in the addition of 1,1,2-tricarbethoxyethane to oct-1-ene there was no change in the product ratio on varying the ratio of the reactants, *i.e.* the preferential removal of one of the chain carrying radicals by telomer formation did not occur. P.m.r. studies at 34° have shown that 1,1,2-tricarbethoxyethane exists entirely in the keto-form even in the presence of excess of oct-1-ene (2 moles).

It appears from these experiments, therefore, that the ratio of the isomeric products formed in the peroxide-induced addition of acetylacetone to oct-1-ene is related to the degree of enolization of the addendum under the conditions of the experiment, *i.e.* we are not dealing with the addition of a single addendum to the olefin but with competitive addition of two addenda, the relative amounts of which vary with the concentration of olefin and the temperature.

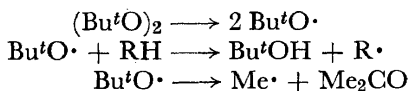
Several factors can be considered to contribute to a rationalization of this novel phenomenon. First, the statistical factor may be important. In the enolic form only one hydrogen atom attached to C₃ will be available for abstraction compared with two in the keto form. At high concentrations of the enol this could lead to the formation of more C₁ radicals, as observed.

Other factors which cannot be ignored are the relative stabilities of the possible enolic and ketonic forms of both C₃ and C₁ radicals [and hence the relative ease of displacement reaction

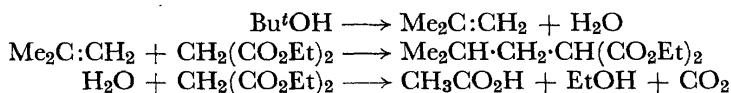


and the relative electrophilicities of these radicals [and hence the relative ease of the addition reaction].

During the course of these experiments involving the addition of compounds containing activated methylene groups to oct-1-ene, attempts were made to estimate the relative ease of abstraction of hydrogen from the methylene groups in the various substrate. The method envisaged was the well known procedure outlined below:



whereby the ratio of *t*-butanol to acetone can be taken to be a measure of the ease of abstraction of hydrogen by the *t*-butoxyl radical. In the case of diethyl malonate, no *t*-butanol was formed at 105° and major products were diethyl isobutylmalonate and ethyl acetate. The simplest explanation of these observations involves complete dehydration of *t*-butanol to 2-methylpropene followed by radical chain addition of diethyl malonate to the olefin, thus:



Against this explanation however are the observations that (a) *added t*-butanol is not completely consumed in an otherwise identical reaction and (b) ethyl acetoacetate, under the same conditions, does not give ethyl isobutylacetoacetate, although it has been shown that the radical addition of ethyl acetoacetate to alkenes occurs at approximately the same rate as the corresponding addition of diethyl malonate.

This reaction is analogous to that reported by Fields and Rolih⁸ who noted the formation of diethyl isobutylphosphonate in the reaction of diethyl phosphonate with *t*-butyl peroxide in benzene.

ARYLATION

Amyl nitrite and aromatic primary amines for *in situ* arylation

This process can be said to be a variation of the Gomberg reaction, which has well known disadvantages arising in part from the heterogeneity of the reaction medium. We have shown that the reaction of aromatic amines with amyl nitrite in aromatic solvents conveniently leads in many cases to good yields of the corresponding biaryl (*Table 3*) the main by-products being amyl alcohol and water⁹. The simplicity of this reaction makes it potentially one of the best routes to biaryls so far reported. A similar reaction was recently reported by Shu Huang¹⁰.

Table 3. Aromatic arylation using amyl nitrite and amines
 $\text{ArNH}_2 + \text{AmONO} + \text{PhH} \rightarrow \text{ArPh} + \text{AmOH} + \text{N}_2 + \text{H}_2\text{O}$

<i>Amine</i>	<i>Biaryl (%)</i>
Aniline	Biphenyl (50)
<i>p</i> -Chloroaniline	4-Chlorobiphenyl (53)
<i>p</i> -Anisidine	4-Methoxybiphenyl (33)
3-Aminopyridine	3-Phenylpyridine (52)
3-Aminoquinoline	3-Phenylquinoline (35)
<i>o</i> -Chloroaniline	2-Chlorobiphenyl (44)
<i>p</i> -Iodoaniline	4-Iodobiphenyl (26)
<i>o</i> -Toluidine	2-Methylbiphenyl (27)
<i>o</i> -Phenylenediamine	Benzotriazole (79)
<i>o-t</i> -Butylaniline	2- <i>t</i> -Butylbiphenyl (trace)
<i>o</i> -Nitroaniline + mesitylene	2,4,6-Trimethyl-2'-nitrobiphenyl (40)

Additional noteworthy points, to which we will refer later, connected with the results summarized in *Table 3* are the very low yield of 2-*t*-butylbiphenyl obtained from *o-t*-butylaniline, and the formation of a significant quantity (0.1 mole/mole of amine) of *p*-di-iodobenzene in the reaction of *p*-iodoaniline.

That the reaction is homolytic is indicated by comparison of the ratio of isomeric chlorobiphenyls obtained on phenylation of chlorobenzene by amyl nitrite and aniline, with those obtained by other established radical routes (*Table 4*)¹¹. The precise mechanism of the reaction is still to be established and it is possible that a process similar to that described by R chardt¹² for the Gomberg reaction is occurring.

A useful extension of this *in situ* diazotization involves the reaction of

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Table 4. Phenylation of chlorobenzene

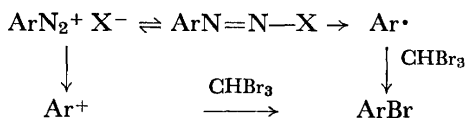
Reagent	Temperature (°C)	Composition (%) of chlorobiphenyl mixture		
		<i>o</i>	<i>m</i>	<i>p</i>
(PhCO ₂) ₂	70	54	31	15
(PhCO ₂) ₂	80	50	32	18
Gomberg	5	65	22	13
Nitrosoacetanilide	20-25	56	28	16
Phenylazotriphenylmethane	45	58	28	14
Silver iodide dibenzoate	130	60	24	16
Phenylhydrazine + Ag ₂ O	0	65	22	13
Diazoaminobenzene + heat	130	60	24	16
PhNH ₂ + AmONO	100	55	27.5	17.5

amyl nitrite and aromatic amines in polyhalogenomethanes (Table 5)¹¹. Thus in the case of bromoform a very useful alternative to the Sandmeyer bromination reaction emerges.

 Table 5. Reactions of ArNH₂ with amyl nitrite in CHBr₃

X in X·C ₆ H ₄ ·NH ₂	ArBr (%)
4-Br	67
3-NO ₂	60
4-NO ₂	73
4-MeO	51
2,4-(NO ₂) ₂	49
2-CO ₂ Et	71
3-NH ₂ pyridine	39

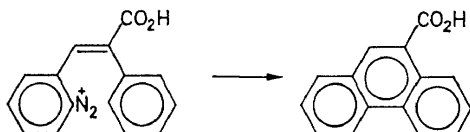
The mechanism of this reaction has also to be established and it is by no means certain that the process is entirely homolytic. It is possible that some, at least, of the aryl bromide is arising by an ionic process as well as by radical abstraction. Thus such a dual mode of decomposition might account for



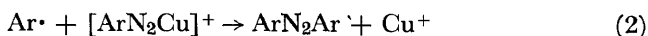
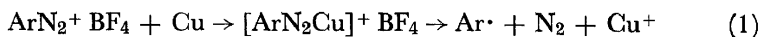
some of the anomalous results which have been recorded for the decompositions of *N*-nitrosoacetanilide and diazohydroxides in solvents such as chloroform and bromotrichloromethane^{11, 13}, which give rise to abstraction of both chlorine and hydrogen in the former and both bromine and chlorine in the latter, whereas phenyl radicals generated from benzoyl peroxide and phenylazotriphenylmethane abstraction only hydrogen and bromine.

Copper induced decompositions of diazonium fluoroborates

The Pschorr internuclear cyclization and related reactions, exemplified by the following conversion, is known to proceed in the presence of copper



powder almost certainly by a radical route, or thermally in acid solution by heterolysis. In an attempt to confirm the radical nature of the copper initiated reaction, and in so doing possibly to produce a convenient route to biaryls, we have investigated the reaction of simple aromatic diazonium fluoroborates with copper powder in the presence of aromatic solvents. Following the suggestions of Waters¹⁴ and Kochi¹⁵ concerning the mechanisms of the Sandmeyer reaction it was anticipated that a series of one-electron redox reactions would occur to give aryl radicals which would arylate the solvent and/or react with the diazonium cation in association with copper to give the corresponding azo compound.



In practice, reaction occurred at room temperature only after the addition of acetone as a solubilizing agent (10 per cent v/v) to the aromatic solvent, whereupon nitrogen was vigorously evolved and a flocculent red precipitate of a complex of the azo compound with cuprous fluoroborate was formed. A small quantity of the free azo compound, and of the biaryl (ArPh) were also formed. The complex readily decomposed on treatment with water or polar solvents to give the azo compound, cupric fluoroborate and copper. It appeared therefore that reaction according to (1) and (2) was predominant, i.e. the postulated intermediate diazonium copper-cation under these conditions acts as an efficient trap for aryl radicals produced by one electron transfer.

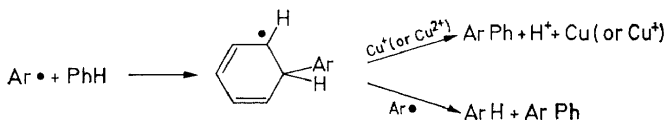
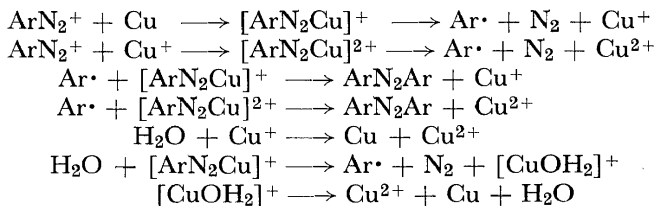
The addition of water to the system by the use of wet diazonium fluoroborate led to quite different results. In this case the azo complex was not formed, neither was it a precursor, and the major product was the biaryl, together with the reduction product of the diazonium salt (ArH) and the corresponding phenol. The use of a hydrated salt such as magnesium sulphate hydrate or hydrated sodium sulphate, remarkably, in view of the heterogeneity of the reaction, gave similar results. Measurement of the nitrogen evolved under various conditions established that the reaction in the absence of water required one g atom of copper for complete evolution of nitrogen (0.5 mole). While the reaction in the presence of water requires almost catalytic amounts of copper (0.1–0.3 g atom) for evolution of the theoretical amount of nitrogen (0.8–1.0 mole).

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Comparison of the isomer ratios produced in arylation of nitrobenzene and fluorobenzene by diazonium fluoroborates in the presence of copper and hydrated salts with those produced from authentic sources of aryl radicals confirmed the radical nature of the reaction.

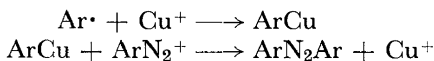
These results allow the following tentative reaction scheme to be suggested, which has much in common with those postulated by Waters¹⁴, and Kochi¹⁵ for reactions such as the Meerwein and Sandmeyer.

Reactions of ArN_2BF_4 in the presence of copper



The function of water in the reaction is therefore assumed to be twofold: (a) to suppress the amount of Cu^+ present, and hence the formation of the azo compound (it is known that the rate of formation of the azo arene is dependent on $[Cu^+]^2$: Cowdrey and Davies¹⁴), (b) to induce decomposition of the intermediate diazonium-copper cation [reaction (4)] which will also lead to a reduction of the concentration of cuprous ions. The mode of formation of the phenol is obscure but it is possible that ligand radical transfer of water, as suggested by Cohen and Lewin¹⁶ might be occurring or that interaction of phenyl radicals with oxygen, as suggested by Kochi¹⁵ and by Simamura¹⁷, might be taking place.

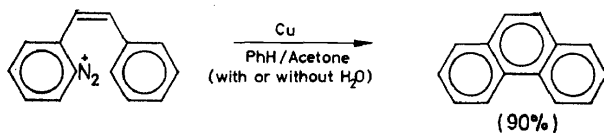
An alternative route could involve the intermediacy of aryl copper derivatives.



Our experiments included acetone, however, which we would have expected, with Kochi¹⁵, to react with aryl copper to give carbinols. Until further evidence is produced we are therefore prepared to accept the above variation of the Waters mechanism as a reasonable rationalization of this series of reactions.

Turning now to the Pschorr reaction it might be expected from the foregoing that 2-diazonium-*cis*-stilbene fluoroborate would behave differently on treatment with copper powder in benzene in the presence and absence of water. In both cases, however, ring closure occurred in high yield, indicating steric preference for ring closure rather than formation of azoarene,

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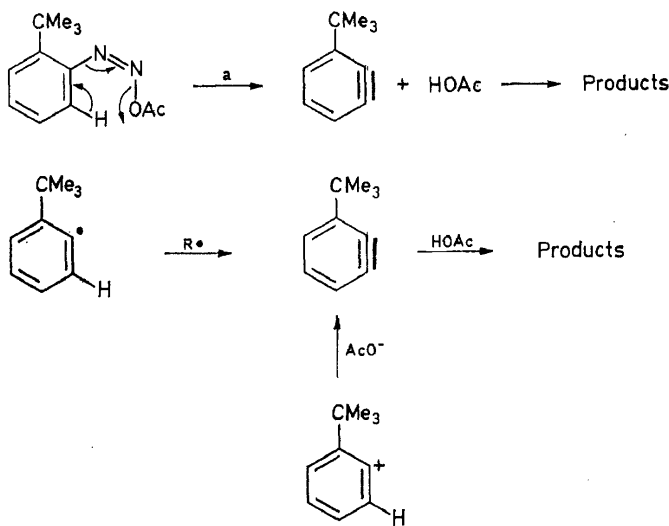


which involves a reaction between two bulky moieties $\{\text{Ar}^\bullet + [\text{ArN}_2\text{Cu}]^+\}$. In accord with this, reaction of the *trans*-analogue, *trans*-2-diazostilbene, which is not subject to the same steric factors, gave the expected products: reaction with copper in benzene in the absence of water gave an azo complex while that in the presence of water gave rise to phenylation of the solvent without the formation of the azo compound.

Anomalous reactions of nitrosoacylarylamines

The rearrangement and decomposition of *N*-nitrosoacylarylamines, such as *N*-nitrosoacetanilide, in aromatic solvents is a well known method of homolytic aromatic substitution¹⁸. Although this reaction gives a good yield of the required biaryl in the case of *p*-*t*-butyl *N*-nitrosoacetanilide in benzene, it fails in the case of the *ortho* isomer¹⁹. In this case the main products are *o*- and *m*-*t*-butylphenyl acetates (46 per cent), and a trace only of 2-*t*-butylphenyl is formed. The formation of the acetates suggested the intermediacy of an aryne, a supposition confirmed by a trapping experiment with anthracene which gave rise to the corresponding triptycene. 2,5-Di-*t*-butyl-*N*-nitrosoacetanilide behaves similarly.

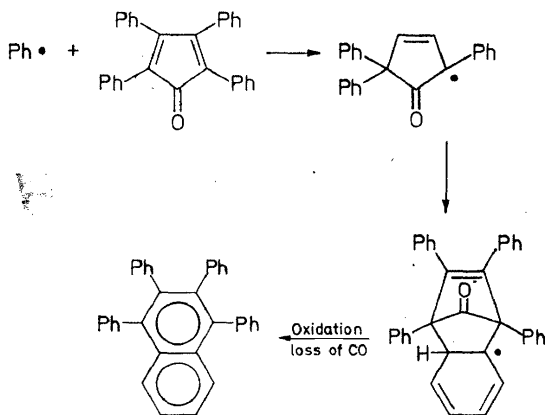
The low yield of 2-*t*-butylbiphenyl suggests that steric factors are important, thus suppressing the normal pattern of reaction and allowing otherwise unfavourable reactions to occur. Possible reaction paths include a concerted decomposition of the isomeric diazo acetate (a), which would need to be in the *cis* form (b) a stepwise decomposition which could be homolytic or heterolytic.



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Our current investigation, as yet incomplete, of the mechanism of this novel reaction has involved a study of the dependence of aryne formation versus normal radical decomposition on the nature of substituent groups in the ring. During this study two striking and unexpected observations have been made.

The first involved the isolation of 1,2,3,4-tetraphenylnaphthalene (17 per cent) from the decomposition of unsubstituted *N*-nitrosoacetanilide in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone. An observation of this type has so far invariably been taken as evidence for the participation of benzyne. In view of the undoubted presence of free phenyl radicals in the system it was possible that this product has arisen in this case by the reaction of phenyl radicals with tetracyclone.

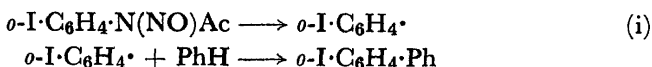


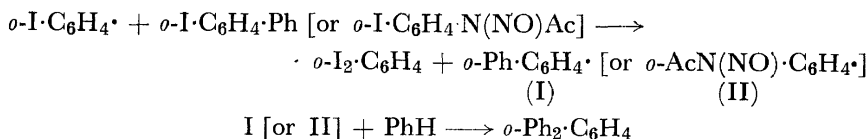
A reaction carried out using phenylazotriphenylmethane in place of *N*-nitrosoacetanilide, however, gave no 1,2,3,4-tetraphenylnaphthalene.

The full mechanistic implications of these observations have still to be determined but it is clear that at this stage a benzynoid contribution to the reaction path cannot be discounted.

The second unexpected observation²⁰ in this series of experiments involved the formation of *o*-di-iodobenzene (12 per cent) and *o*-terphenyl, in addition to the expected 2-iodobiphenyl, as a result of the decomposition of *o*-iodo-*N*-nitrosoacetanilide in benzene. A reaction carried out in the presence of 2,3,4,5-tetraphenylcyclopentadienone gave, as an additional product, 1,2,3,4-tetraphenylnaphthalene (by m.p. and mixed m.p. and correct i.r. spectrum), indicative of the intermediacy of benzyne (*c.* 1 per cent). It has been further shown, that *m*- and *p*-iodo-*N*-nitrosoacetanilides in benzene give *m*- and *p*-di-iodobenzenes respectively in addition to the expected 3- and 4-iodobiphenyls. The reaction of the *m*-isomer also yielded *m*-terphenyl, *p*-terphenyl was not sought in the case of the *p*-isomer.

Exemplified by the *o*- case, these results suggest the following:





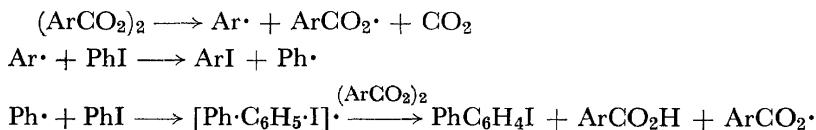
This suggests that aryl radicals have a high affinity for iodine in aromatic iodides, a supposition supported by the following observations:

(a) the decomposition of substituted benzoyl peroxides, not containing iodine, (e.g. 4-Cl, 4-Br, 3-Br, 4-Me, 2-Br) or of *p*-chloro-*N*-nitrosoacetanilide, in iodobenzene gave significant yields (0.6–0.95 mole/mole) of the corresponding aryl iodide together with mixtures of 2-, 3-, and 4-iodobiphenyls (30–70 per cent based on the aryl iodide), of isomeric composition expected from radical phenylation of iodobenzene (e.g. 56 per cent 2-; 26 per cent 3-; 18 per cent 4-iodobiphenyl). The corresponding benzoic acids (*c.* 0.8 mole/mole) were also formed in the reactions of the peroxides.

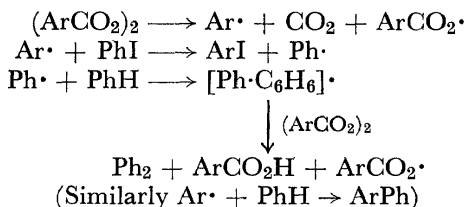
(b) Significant amounts of *p*-chloro- and *p*-bromo-iodobenzene (0.37, 0.36 mole/mole) have been isolated from reactions of *p*-chloro-*N*-nitrosoacetanilide (1 mole) and *p*-bromobenzoyl peroxide (0.5 mole) respectively in benzene (20 mole) admixed with iodobenzene (1 mole). Other products included 4-bromo- and 4-chlorobiphenyl, and, in each case, biphenyl.

(c) *p*-Iodobenzoyl peroxide (1 mole) in benzene (20 mole) gives *p*-di-iodobenzene and *p*-terphenyl in addition to the expected 4-iodobiphenyl.

The formation of phenyl radicals in (a) above, suggests participation of the following sequence, or one similar in the case of *p*-chloro-*N*-nitrosoacetanilide, in the case of the decompositions of aryl peroxides in the presence of iodobenzene.



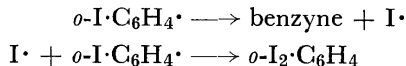
Reactions described under (b) and (c), in which the iodo compound is initially present in high dilution in benzene further emphasize the ease of the transfer process. Thus in (b) a reasonable rationalization includes the following sequence



The formation of a small quantity of benzyne in the case of *o*-iodo-*N*-nitrosoacetanilide could be the result of the loss of an iodine atom from an *o*-iodophenyl radical formed in (i) or the collapse of the intermediate (II), if formed.

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Relevant to these results is the recent report²¹ that decomposition of the related (*N*-2-iodophenyl)-*N*-nitrosobenzamide in benzene gives, in addition to 2-iodo-biphenyl, benzyne (7 per cent) and *o*-di-iodobenzene (18 per cent). The following route was favoured, in which benzyne formation was related directly to that of *o*-di-iodobenzene.



The generality of the iodine abstraction reaction demonstrated by us suggests that it is unnecessary to link the formation of benzyne with that of *o*-di-iodobenzene and that formation of the latter by direct abstraction of iodine by an *o*-iodophenyl radical is more likely.

It should be noted that there is one previous report of a reaction similar to those now reported: Harley-Mason and Mann²² noted without details that a Gomberg reaction of *p*-iodoaniline gave *p*-di-iodobenzene as a side-product. In accord with this is our observation, reported above, of the formation of *p*-di-iodoaniline in the reaction of *p*-iodoaniline with pentyl nitrite in benzene.

Finally it is with great pleasure that I record my gratitude to my colleagues involved in this work: to my teacher, D. H. Hey, F.R.S. who first aroused my interest in this subject and with whom I have been associated for much of the time and to my younger collaborators, namely J. C. Allen, D. Brydon, M. Harger, B. W. Harris, P. G. Hibbert, S. H. Ong, D. A. Roy, J. T. Sharp, M. N. Siddiqui, D. M. Smith and Miss J. Thomson. Without the enthusiasm and skill of these young people, little of this work would have been completed.

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