

Aryl radicals from hexazadienes and tetrazenes

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Aryl radicals are produced from both ends of the hexazadienes **1** and **2** and from the tetrazene **3**, either thermally or photolytically. They attack aromatic compounds in the nucleus, the yield of biaryl being in the range 40–70%, though it can be made nearly quantitative by using *m*-dinitrobenzene as an additive. The aryl radicals also oxidize 2-propanol to acetone, the reduction products being the halogenobenzene and 1,2-diacetylhydrazine.

Photolysis of **1** goes mainly by way of the tetrazene **3**, and this may also be a significant pathway in the thermal reaction. Azodiacetyl is an intermediate in the thermal reaction of **1** with 2-propanol and may be generally so in all its reactions.

Radical induced decomposition is believed to be important in the reactions of **1**, **2**, and **3**, and it is probably responsible for the formation of 1-acetyl-1-arylhydrazines, routinely produced in yields of up to 25%.

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On a préparé des radicaux aryles à partir des deux extrémités des hexadiènes **1** et **2** et à partir du tétrazène **3** soit thermiquement ou photochimiquement. Ils attaquent les composés aromatiques au niveau du noyau, le rendement en dérivés biaryles étant de l'ordre de 40 à 70%. Ce rendement peut être quantitatif si on utilise le *m*-dinitrobenzène comme additif. Les radicaux aryles oxydent également le propanol-2 en acétone, avec comme produits de réduction l'halogénobenzène et la diacétyl-1,2 hydrazine.

La photolyse du composé **1** se fait principalement au moyen du tétrazène **3** et ceci peut constituer également un mécanisme important dans la réaction thermique. L'azodiacétyl est un intermédiaire dans la réaction thermique du composé **1** avec le propanol-2 et il peut en être ainsi dans toutes ses réactions.

On pense que la décomposition induite par les radicaux est importante dans les réactions des composés **1**, **2** et **3** et qu'elle est probablement responsable de la formation des acétyl-1 aryl-1 hydrazines, produits couramment avec des rendements allant jusqu'à 25%.

[Traduit par le journal]

Introduction

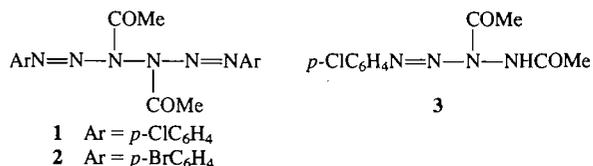
The thermal decomposition of linear N to N unsaturated polyaza compounds, like that of simple azo compounds, is expected to yield radicals. There is a common presumption, which is generally but not invariably true, that the more N atoms there are in the system the less stable it is. Thus polyaza compounds with more than four contiguous N atoms are expected to decompose more easily than tetrazenes or triazenes.

Pentazadienes (**1**), hexazadienes (**2**) (there is no record anywhere of a heptaza compound), and octazatrienes (**3**) have all been known for over 70 years, though since then there have been relatively few references to their chemistry. In many of the reactions described radical pathways are either not involved or are not clearly established. Examples in which nitrogen–nitrogen homolysis has been demonstrated are found for 1,3,5-tri-*p*-tolyl-1,4-pentazadiene both by a product study of its thermolysis in cumene (**4**), and by the observation of a CIDNP effect in CHCl₃ at 70°C (**5**), and for other pentazadienes by their ability to initiate polymerization (**6–8**). Octazatriene homolysis was inferred in the case of 1,8-di-*p*-tolyl-3,6-diphenyl-1,4,7-octazatriene by its reaction with cumene (**9**), and in the case of the tetraphenyl analogue by the successful polymerization of ethylene (**8**).

One hexazadiene has been used as a polymerization initiator (**8**) but, in the only other papers describing this class of compounds (**10**, **11**), no reactions are reported which are unambiguously homolytic in nature.

Recently we carried out a crystal determination on 1,6-di-*p*-chlorophenyl-3,4-diacetyl-1,5-hexazadiene (**1**) (**12**), which showed that its *N*-acetyl groups had an unusually high degree of single bond character in the C to N bond (1.403 Å) and of double bond character in the C to O bond (1.200 Å). This led to the prediction that the acetyl group should be very electrophilic, which was verified by its ability to form esters from alkoxides and phenoxides and acetamide derivatives from primary and secondary amines; the amine reactions showed very high selectivity, particularly to steric factors. In all these and in the hydrolysis reactions described by earlier workers (**10**) heterolytic cleavage of **1** is obviously involved. Since no product studies have been carried out in any reaction of a hexazadiene where homolysis might be likely, we decided to extend our work with **1** in that direction.

We report here on the efficient production of *p*-chloro- and *p*-bromophenyl radicals by thermolysis and photolysis both of the hexazadienes **1** and **2**, and of the tetrazene **3** whose chemistry is interconnected with that of **1** in some of these reactions.



Results and discussion

The hexazadienes **1** and **2**, prepared by the coupling of two equivalents of the diazonium solution with one of diacetylhydrazine (10, 12), are extraordinarily stable once purified. Samples of **1** remain unaffected indefinitely at room temperature, even in an open atmosphere and unprotected from light. Its stability in solution to acids (10) and to hindered secondary amines (12) has been noted. It has a half-life of several hours in refluxing benzene (though it accelerates thereafter), and of almost 5 minutes in refluxing chlorobenzene.

Though 1-aryl-3,4-diacetyl-1-tetrazenes have been implicated as intermediates in the formation of hexazadienes (10), **3** is the first example of such a compound isolated and characterized. It crystallizes as a monohydrate in excellent yield when a solution of *p*-chlorophenyldiazonium chloride is added to a carbonate solution of one equivalent of diacetylhydrazine.¹ It also is stable to ambient conditions but decomposes very much more rapidly in solution than the hexazadienes; immediate and copious evolution of nitrogen is observed when a solution in benzene is heated.

Dilute solutions (usually 0.025 *M*) of **1** or **2** were completely decomposed in refluxing benzene (80°C) or chlorobenzene (131°C), or in bromobenzene (also at 131°C). Quantitative analysis of the yields of the major products, the biaryls and diacetylhydrazine, were determined by high resolution gas-liquid chromatography (glc).

The coupled products obtained in benzene were *p*-chlorobiphenyl from **1** and *p*-bromobiphenyl from **2**. In chlorobenzene **1** and **2** gave all three 4'-halo-chlorobiphenyls and the analogous 4'-halo-bromobiphenyls in bromobenzene. Yields were in the range of 40–70%. The absence of other significant coupling products, and in particular the *o*:*m*:*p* isomer ratios observed in chlorobenzene and bromobenzene, are unmistakably diagnostic of the involvement of *p*-chloro- and *p*-bromophenyl radicals (13, 14).

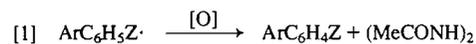
¹It crystallizes out in fact much more rapidly than **1**, which can cause problems in the synthesis of the latter. On occasion we had to resort to making **1** in a laboratory in which **3** had never been prepared or worked with.

The tetrazene **3** was also decomposed (a much faster reaction) in both refluxing benzene and chlorobenzene. The isomer ratios from the latter solvent are again indicative of *p*-chlorophenyl radical reactions, though the *o*-ratio is rather higher and the *p*-ratio lower than in the corresponding reaction of **1** in chlorobenzene (Table 1).

The yields of biaryls and their isomer ratios from thermolysis of **1–3** in chlorobenzene and bromobenzene are shown in Table 1, along with the yields and ratios from related thermolyses to be discussed later.

The following compounds were not detected (<1%, glc) in the pyrolysis reactions: *p*-chlorophenyl azide and 1-*p*-chlorophenyl-3-acetyltri-azene,² *p,p'*-dichloroazobenzene, 1,2-di-*p*-chlorophenylhydrazine, *p*-chloroaniline, *p*-chloroacetanilide, and 1-*p*-chlorophenyl-5-methyltetrazole, an expected hydrolysis product of **3** (10) (by which route it was synthesized), or of 1-*p*-chlorophenyl-4-acetyltetrazene (15).

Since the biaryls and diacetylhydrazine are the major products, the main overall process must be the dehydrogenation of the initially formed aryl-cyclohexadienyl radicals (13, 14) by one or more intermediates containing the *N,N'*-diacetyl fragment (reaction [1]).



A plausible set of steps leading to these products from both the hexazadiene **1** and the tetrazene **3**, are shown in reactions [2]–[12]. Reactions [2]³ and [8] suppose only spontaneous fission of substrate. If induced fission also occurs, as appears to be the case for **1** at least, many other decomposition pathways are possible. Of those leading to biaryls^{4,5} the processes involving the diazanyl radical **6** (from reactions [6] or [8]), or the cyclohexadienyl radical **5** (from reaction [3]) are probably important examples; these are shown in reactions [9]–[12]. Indeed [11] and [12] between them, in chain reac-

²The triazene was shown in a control experiment to be stable to the reaction conditions. These two products are quantitatively formed in the reaction of **1** with nucleophiles (10, 12).

³We reject as unlikely the one-step decomposition of the hexazadiene to 2 Ar· + 2 N₂ + MeCON=NCOME.

⁴Another route to biaryls of course, is the disproportionation of 2 moles of the arylcyclohexadienyl radical to biaryl and cyclohexadiene; this is significant only if oxidation or trapping of the radical cannot intervene (see later discussion).

⁵Attack of Ar· on **1** or **3** would give the symmetrical biaryl. In view of the high reactivity and hence low concentration of such radicals this reaction is unlikely in dilute solution. No *p,p'*-dichlorobiphenyl was obtained when **1** was decomposed in benzene.

TABLE 1. Yields (%) of products of thermolysis of 1, 2, and 3 in various solvents

Reagent	Solvent	Yield ^a	Biaryl			(MeCONH) ₂ ^b	COME ^{b,c} ARNNH ₂ 9	Other
			<i>o</i>	<i>m</i>	<i>p</i>			
1	C ₆ H ₆	62					13	
	C ₆ H ₅ Cl	67	50.5	27.7	21.8	60	27	
	C ₆ H ₅ Br							
	(i) untreated	60	51.1	31.3	17.6		25	
	(ii) added <i>m</i> -C ₆ H ₄ (NO ₂) ₂	93	53.9	28.3	17.8	>90	<5	
	(iii) N ₂	25	58.9	25.5	15.6		9	
	(iv) O ₂	38	56.4	27.4	16.2			
	C ₆ H ₅ I		52.6	30.5	16.9			
	C ₆ H ₅ Me		53.2	23.5	23.3			PhCH ₂ CH ₂ Ph ^d
	(C ₆ H ₅) ₂		43.8	25.1	31.1			
	C ₆ H ₅ OMe							
	(i) untreated		62.5	18.2	19.3			
	(ii) 1 equiv. AlCl ₃ added		63.9	19.6	16.5			
	None							
	(i) glc injection		0.9		100			C ₆ H ₅ Cl(8)
(ii) sand reaction		0.4		100				
Me ₂ CHOH					99	Trace	Me ₂ CO, C ₆ H ₅ Cl (81), <i>p</i> -ClC ₆ H ₄ N ₃ (0.2)	
2	C ₆ H ₅ Cl	49	53.3	29.4	17.3			
	C ₆ H ₅ Br	77	53.3	29.2	17.5			
	C ₆ H ₅ I		50.9	30.8	18.3			
	None: glc injection	1.7			100			C ₆ H ₅ Br (7)
	Me ₂ CHOH							C ₆ H ₅ Br (90)
3	C ₆ H ₅ Cl	60	61.2	24.6	14.2			

^aBased on [ArN=NN(COMe)]₂ + 2 C₆H₅Z → 2 ArC₆H₄Z and on ArN=NN(COMe)NHCOMe + C₆H₅Z → ArC₆H₄Z.

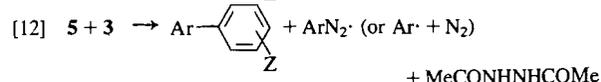
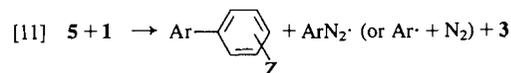
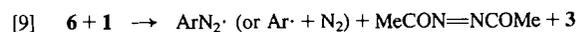
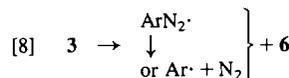
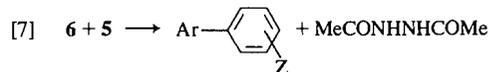
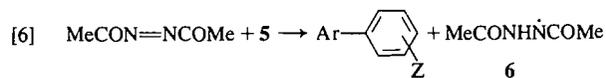
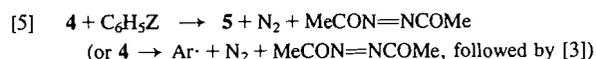
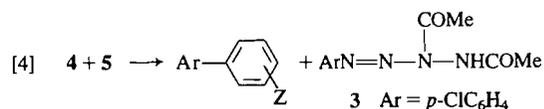
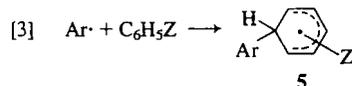
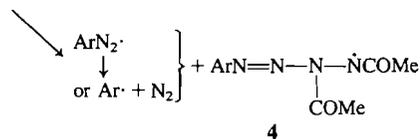
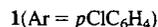
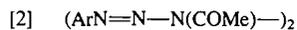
^bNot routinely estimated, but always present.

^cBased on [ArN=NN(COMe)]₂ → ArN(COMe)NH₂.

^d<3% of total yield of *p*-chloromethylbiphenyls.

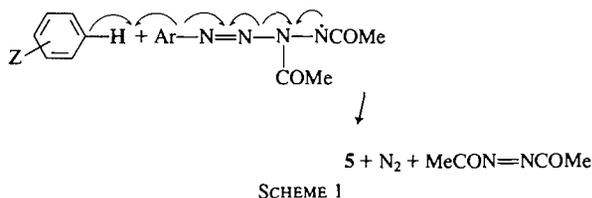
tions together with [3], could account completely for the formation of biaryl from 1 and 3.

The spontaneous or induced decomposition of 1 or 3 (reactions [2], [8], [9], [11], [12]) produces aryl radicals, directly if loss of N₂ is concerted with fission, or otherwise by way of unstable aryldiaz-enyl radicals ArN₂[•]. Evidence in favour of the latter can be found in the decomposition of 1,3,5-tri-*p*-tolyl-1,4-pentazadiene (5). If the radicals ArN₂[•] are involved we assume that loss of N₂ precedes attack on the solvent by reaction [3].



Certainly they do not attack the solvent to form N to C bonds, since neither azo compounds nor the related diarylhydrazines were detected in the reactions.

Reaction [3] normally provides the only route to the cyclohexadienyl radical **5** in radical arylations, but reaction [5] suggests another mechanism by which formation of **5** might become possible, the driving force being the creation of two stable molecules (Scheme 1). This could be a concerted reaction between **4** and ArH (Scheme 1), or a two-step process with **4** first decomposing to the aryl radical, followed by reaction [3].



The oxidation of **5** to biaryl can take place either by a neutral molecule or by encounter with another radical. An example of the former is reaction [6], in which the dehydrogenating power of an azodicarbonyl compound is utilized. So too are reactions [11] and [12], in the induced decomposition, the radical source (**1** or **3**) being the oxidizing agent. The analogous oxidation of the phenylcyclohexadienyl radical by benzoyl peroxide in benzene has been shown to be significant even in dilute solution (16). Oxidation of **5** by another radical is exemplified by reactions [4] and [7]. Processes of this type are very important in radical arylations where induced decomposition of the radical source is absent. They have ample precedent in the unimolecular decomposition of diaryl peroxides in aromatic solvents (13, 14, 16).

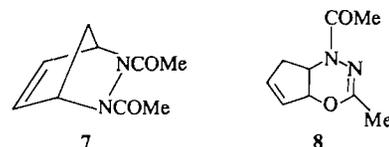
Examination of reactions [2]–[12] shows that two stable intermediates have been invoked, the tetrazene **3** and azodiacyl. These may, but need not, be independent of each other. For example, in the unimolecular decomposition of **1** the sequence [2], [4], [8], [7], and in its induced decomposition the sequence [11], [12], involve only **3**. Similarly azodiacyl only is produced in the sequence [2], [5], [6], [7] when **1** decomposes unimolecularly. Reaction [9] of course produces both, as do sequences like [2], [4], [5], [6]. In the decomposition of **3** azodiacyl could be involved, as in sequence [8], [10], [5].

While both intermediates are probably involved in thermolysis of **1**, we believe azodiacyl is of greater importance than the tetrazene.

This choice is made on the basis of the different

isomer ratios found in the thermolysis of **1** and **3** in chlorobenzene. The tetrazene **3** gives *o* and *p* ratios of 61 and 14% and a total dichlorobiphenyl yield of 60%. If the thermolysis of **1**, which gives *o* and *p* ratios of 51 and 22% and a total biaryl yield of 67%, goes only by way of **3**, and the latter again gives a 60% biaryl yield, then it follows that the first oxidation step in the thermolysis (reaction [4] in the sequence [2], [3], [4]) affords an *o* and *p* ratio of 43 and 29%. This amount of divergence from the normal spread of *o/p* ratios, produced by other sources of aryl radicals, has not been observed in any other work and we regard it as quite unlikely.⁶

We tried to detect the intermediacy of azodiacyl by allowing a solution of **1** in refluxing chlorobenzene to decompose in the presence of a large excess of cyclopentadiene, in the hope that the latter might trap the azo compound as its known adduct **7** (17). Much polymeric material from the diene was formed, and a reduced yield of biaryl, but no trace of **7** or its product of thermal rearrangement **8** (17) could be detected by glc analysis. Azodiacyl is evidently more efficiently trapped by **5** than by the diene at this temperature. Using the diene, however, in the reaction of **1** with 2-propanol at 83°C (described below), the involvement of azodiacyl was established, and so it is reasonable that it can also be an intermediate in the reactions in aromatic solvents.



Photolysis of **1** or **3** also yields aryl radicals. Decomposition in benzene or chlorobenzene at 10°C with a medium pressure mercury lamp gave diacylhydrazine and biaryl; the yields and isomer ratios are shown in Table 2. The lower temperature allowed the reaction of **1** to be monitored by ¹H nmr spectroscopy for the presence of the thermally labile azodiacyl or tetrazene. While the former could not be conclusively detected, the tetrazene was seen to be the major coproduct of the first arylation step, an observation consistent with the closeness of the isomer ratios in the photolysis of **1** and **3** in chlorobenzene (cf. the thermolysis results). Concentrations of **3** greater than 60% of theoretical (determined by ¹H nmr analysis) were obtained before separation of solids made further analysis

⁶The spread of ratios between **1** and **3** is quite large but is within the range observed in arylations with different radical sources in other reported work (14).

TABLE 2. Yields (%) of products^a of photolysis^b of 1 and 3 in benzene and chlorobenzene

Reagent	Solvent	Yield ^c	Biaryl		
			Isomer ratios		
			<i>o</i>	<i>m</i>	<i>p</i>
1	C ₆ H ₆	65			
	C ₆ H ₅ Cl	43	62.7	24.4	12.9
3	C ₆ H ₆	82			
	C ₆ H ₅ Cl	48	66.5	21.0	12.5

^a1,2-Diacetylhydrazine and 1-acetyl-1-arylhydrazine also produced but yields not determined.

^b450 W lamp.

^cMeasured as for Table 1.

unreliable (Table 3). Work-up of a partially reacted solution gave a slightly impure sample of 3.

Though the yields of biaryls in the reactions described were moderate to good they showed some degree of variation among themselves, even with duplicate runs on the same system.⁷ A limiting factor in the success of the reaction is, of course, the ability of the cyclohexadienyl radical 5 to get oxidized to biaryl before it either disproportionates to the cyclohexadiene and biaryl or couples to the tetrahydroquaterphenyl (13, 14). This problem has been addressed in great detail in diaryl peroxide chemistry, particularly by Hey and by Williams, and their co-workers. They found that a range of N=O containing additives (nitrobenzene, *m*-dinitrobenzene, nitrosobenzene, azoxybenzene) greatly improved the yield of biaryl and aroic acid (the coproduct of the oxidation-reduction), without being chemically changed themselves (18, 19). The use of nitrobenzene in the decomposition of benzoyl peroxide in benzene was examined in detail (19). It was shown that "the nitro group effect" operates by trapping the very reactive phenylcyclohexadienyl radical, probably by σ -bond addition

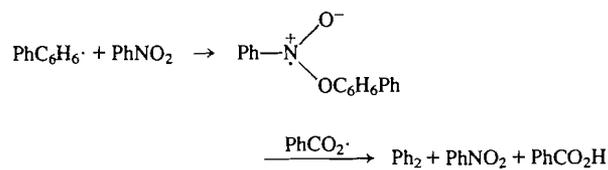
TABLE 3. Proportions (%)^a of 1, 3, and other Me-containing products from photolysis^b of 1 in benzene

Initial [1]	Time (min)	1	3	Other
0.26 M	10	84	12	4
	25	81	14	5
	45	68	25	7
	62	64	27	9
	90	44	39	17
0.13 M	10	75	21	4
	25	63	29	8
	62	17	63	20

^aDetermined by integration of Me region of ¹H nmr spectrum.

^b100 W lamp.

⁷The isomer ratios, however, remained constant ($\pm 1.6\%$).



SCHEME 2

at nitro oxygen (Scheme 2), the new, more stable, radical being capable of survival till encounter with the benzoyloxy radical gives benzoic acid, biphenyl, and recovered nitrobenzene.

This approach to optimizing yields has not to our knowledge been applied to arylations from radical sources other than peroxides, but the principle should be equally applicable. In reactions of 1, radicals such as 4 and 6 take the place of the benzoyloxy radical. We repeated the thermolysis of 1 in bromobenzene with 0.67 molar equivalent of *m*-dinitrobenzene and obtained yields of >90% of both the chlorobromobiphenyls and diacetylhydrazine.

The isomer ratio was not significantly changed and is thus independent of yield, a point firmly established in peroxide work (20). Gas-liquid chromatography showed that the dinitrobenzene was recovered, and though its amount was not measured, the nearly quantitative nature of the arylation establishes that its role must again have been strictly catalytic. This result suggests that reactions like [4] and [7] are important, and that induced decomposition alone (reactions [11], [12]) cannot be responsible for biaryl formation.

Degassing the solution and maintenance of a nitrogen atmosphere during the decomposition of 1 in bromobenzene caused a large reduction in the yield of biaryl, with an increase in the amount of material appearing in the late stages of the chromatogram. Thus oxygen has a beneficial effect in the reactions in untreated solvents, explaining the slight variations of yields in the latter. High oxygen levels were deleterious, since decomposition of 1 in bromobenzene in the presence of the dispersed gas gave a reduction in yield and the appearance of many new products in the chromatogram. This result is at variance with others involving diaryl peroxides (20, 21), where a dramatic increase in biaryl yields and a reduction of side products was clearly demonstrated. Oxidative degradation of 1 is presumably a competing process.

The hexazadienes were also decomposed in other representative monosubstituted benzenes. Isomer ratios were determined, but not yields, though glc again showed that in all cases the biaryls and diacetylhydrazine were by far the major products. These results are also shown in Table 1.

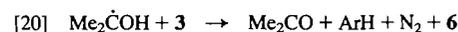
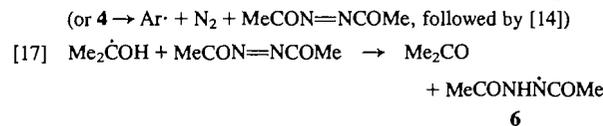
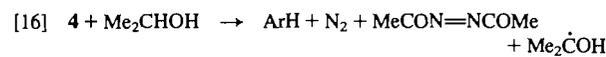
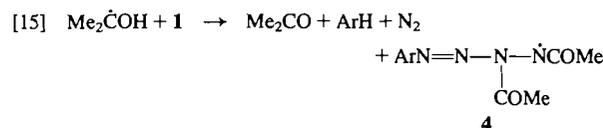
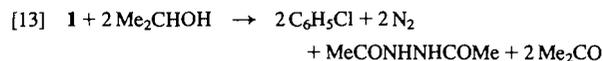
Both **1** and **2** gave very similar results in iodobenzene; there is a notable absence of any steric effect, even for attack of the *p*-bromophenyl radical at the *o*-position. A similar isomer distribution is reported in the decomposition of the corresponding diaryl peroxides in iodobenzene, but radical displacement of iodine was also observed leading to the aryl iodides (**22**). We did not look for these in our reactions.

In the reaction of **1** in toluene there was very little side chain attack, less than 5% of that of ring substitution where the isomer ratios were similar to those observed in the halogenated benzenes. *p*-Chlorobenzoyl peroxide attacks the side chain of toluene more extensively (11%), but substitution ratios have not been reported (**23**). In biphenyl **1** gave the expected monochloroterphenyls, in a ratio predictably low in the *o*-isomer, and similar to that found in the benzoyl peroxide reaction (**24**).

In our earlier work with **1** it was shown to be a mild and selective acetylating agent for primary and secondary amines (**12**). We considered that it might also function as an acetylating agent towards an electron-rich aromatic nucleus in the presence of a Friedel-Crafts catalyst. In fact with anisole containing AlCl_3 there was no evidence of the formation of methoxyacetophenones. The methoxybiphenyls were produced in the normal free radical ratio, similarly observed without the catalyst and noted by others (**20**).

2-Propanol was chosen as a readily oxidizable solvent in which **1** might be expected to react readily by aryl (or other) radical abstraction. The oxidation of ethanol by **1** has already been demonstrated, though a mechanism was not determined (**10**). Radical oxidation of 2-propanol has been effected by benzoyl peroxide, both phenyl and benzoyloxy radicals being involved (**25**), as well as by other radical sources (**26**, **27**). Reaction of **1** was rapid at the bp of the alcohol, giving acetone (not estimated), chlorobenzene (81%), and diacetylhydrazine (99%). Similar reaction of **2** gave bromobenzene (90%). Since the products are equally consistent with an ionic mechanism, we tried to prove the involvement of radicals by repeating the oxidation in an equimolar mixture of alcohol and chlorobenzene. A low yield (21%) of the three dichlorobiphenyls was obtained in the normal isomer ratio for radical attack.⁸ Since this isomer mixture was rapidly obtained at a temperature (83°C) at which **1** itself reacts very slowly, the presumption is that

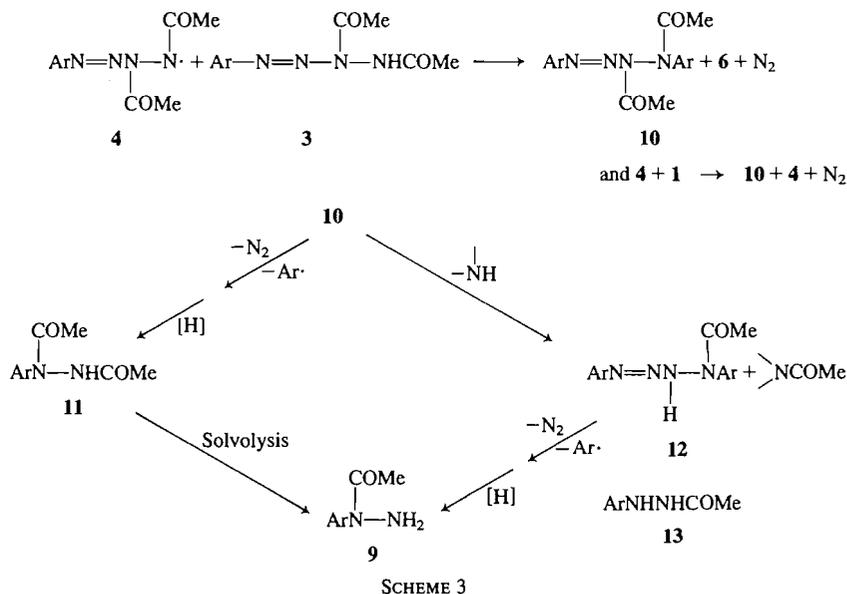
p-chlorophenyl radicals are generated by reaction with the alcohol. The stoichiometry of the oxidation is thus described by [13] and the mechanism must operate mainly by induced decomposition. Reasonable sets of steps are shown in reactions [14]–[20].



Initiation by, for example, the aryl radicals (reaction [14]) gives the 2-hydroxy-2-propyl radical which with **1** gives **4**, but which is regenerated by reaction of **4** with alcohol (reaction [16], in a one- or two-step process). The sequence [15], [16] is thus a chain process completing the reduction of both equivalents of aryl radicals and the oxidation of one equivalent of alcohol. The other product, azodiacyl, completes the oxidation of alcohol by the repeating sequence [17], [18] which involves the radical **6**. Alternatively **4** can react with alcohol to give **3** and the 2-hydroxy-2-propyl radical (reaction [19]); these react to product and **6**, which with alcohol completes the chain (reactions [20], [18]). Thus a sequence involving azodiacyl ([15]–[18]) or one involving tetrazene ([15], [19], [20], [18]) is possible, but we made no attempt to assess the relative contributions of these. However, we were able to confirm the involvement of azodiacyl at least, by repeating the oxidation in the presence of cyclopentadiene. The glc analysis of the products showed the formation of both the adduct **7** and its thermal isomer **8**. The amounts were not estimated.

Consistently reported in yields of 10–25% in Tables 1, 2, and 3 is the formation of 1-acetyl-1-*p*-chloro(or -bromo)phenylhydrazine (**9**) in thermal and photolytic reactions of **1**, **2**, or **3**. It was absent, or almost so, only in the reaction of **1** with 2-propanol, and with chlorobenzene in the presence of *m*-dinitrobenzene, where the yields of

⁸Even in the absence of added chlorobenzene the amount generated in the alcohol oxidation was sufficient to allow the formation of a detectable mixture of the dichlorobiphenyls.



SCHEME 3

chlorophenyl-containing products were very high.

No obvious simple pathway to this product is apparent, involving as it does overall aryl migration to an acetyl-bearing nitrogen, followed by *N*-acetyl cleavage β to the aryl group. Spontaneous aryl migration in **1** or **3** is possible but is much less likely than an intermolecular aryl transfer from **1** or **3** to a suitable *N,N'*-diacetyl containing nitrogen-centred radical. By far the best candidate is the radical **4** and we propose that the key intermediate generated is the (presumably) unstable 1,4-diaryl-3,4-diacetyl-1-tetrazene (**10**). Its formation from **4** and possible reactions leading from it to **9** are shown in Scheme 3.

A sequence of spontaneous or induced homolysis of **10**, followed by hydrogen abstraction by the resulting radical $\text{ArN}(\text{COMe})\text{NCOMe}$, would give the *N,N'*-diacetylarlyhydrazine (**11**). However, **11** does not seem a probable precursor for **9**. It is difficult to imagine a mechanism for the transformation $\mathbf{11} \rightarrow \mathbf{9}$ except one of selective solvolysis, which would require a more reactive nucleophile than any likely to be present in the reaction.

We propose that deacetylation of **10** occurs directly to give **12**. The acetyl group on the nitrogen α to the azo group is expected to be highly electrophilic (**12**), and a mild nucleophile should be capable of displacing it. The nucleophile must be a basic nitrogen derivative, though certainly not *p*-chloroaniline, since both it and its acetyl derivative were not reaction products.⁹ Conversion of **12**

$\rightarrow \mathbf{9}^{10}$ would again involve radical decomposition and hydrogen abstraction of the resulting radical $\text{ArN}(\text{COMe})\text{NH}^{\cdot}$.

Since **9** is the only reaction product containing both the aryl and diacetylhydrazine fragments we thought that it might be the major product when **1** was decomposed in the absence of solvent. Injection of an ethereal solution of **1** in the inlet of the gas chromatogram (250°C, a temperature at which **1** explodes in the condensed state) indeed gave **9** (25%) as well as diacetylhydrazine (24%) as by far the major simple products, though the yield is no greater than in other decomposition reactions. Chlorobenzene (8%), not otherwise routinely tested for, was also a product; so too was *p,p'*-dichlorobiphenyl, in very low yield, but significantly free of the *o*- or *m*-isomers. It must arise by the induced decomposition: $p\text{-ClC}_6\text{H}_4^{\cdot} + \mathbf{1} \rightarrow (p\text{-ClC}_6\text{H}_4)_2 + \text{N}_2 + \mathbf{4}$. Pyrolysis of **1** at 150°C, dispersed thinly on the surface of sand, gave an almost identical result.

Though we have not succeeded in isolating **9**, its identity has been clearly established. Work-up of the photolysate of **1** in benzene gave a fraction very rich in **9** (glc). The ¹H nmr of this fraction showed a strong absorption in the acetyl region as well as the expected *p*-chlorophenyl splitting pattern. A gc-ms analysis showed it had a mol. wt. of 184 (based

¹⁰The alternative decomposition of $\mathbf{12} \rightarrow \text{ArN}_3 + \text{ArNHCOMe}$ would be analogous to the solvolysis pathway observed for **1** with bases to give $\text{ArN}_3 + \text{ArN}=\text{NNHCOMe}$ (**10**, **12**). However, in the latter reaction the triazenylium anion is the leaving group and has a resonance stabilization not matched by the anilide anion.

⁹A variety of basic products may be involved since no other peak of major significance in the glc chromatogram was unaccounted for.

on ^{35}Cl), one Cl atom (isotope ratio), and one acetyl group (strong $M - 42$ peaks); the products from the sand pyrolysis also showed a very intense peak at m/e 184. We were able to rule out the other monoacetyl isomer **13**, since an authentic sample of it had a shorter glc retention time, thus confirming the structure as **9**. An attempt to synthesize **9**, by acetylation of 1-*p*-chlorophenyl-2-formylhydrazine followed by acid hydrolysis, gave a mixture of mono and diacyl *p*-chlorophenylhydrazines of which **9** was one (glc coinjection with a pyrolysis reaction mixture).

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-10 spectrometer. Nuclear magnetic resonance spectra were obtained on a Perkin-Elmer R12B (^1H) or a Bruker WP-80 (^1H , ^{13}C) spectrometer, and are referred against internal tetramethylsilane. All gas-liquid chromatographic analyses were carried out on a Hewlett-Packard 5830 or 5840A Chromatograph with flame ionization detection and He or N_2 as carrier gas; glass columns 6 ft \times 1/8 in. id with an Aue packing of Carbowax 20M on Chromosorb W were used. Gas chromatographic - mass spectrometric measurements were made on a Hewlett-Packard 5992 instrument. Conventional mass spectra were run on a Varian MAT-CH7.

Starting materials and reference compounds

Solvents were dried by conventional methods, but were not degassed for most routine decompositions. For reactions done in the absence of oxygen the solvent was first refluxed to expel all gases and an atmosphere of N_2 then maintained during the decomposition.

Hexazadienes **1** and **2**

These were prepared as described earlier (10, 12).

1-*p*-Chlorophenyl-3,4-diacetyl-1-tetrazene (**3**)

A freshly prepared solution (150 mL) of *p*-chlorophenyl-diazonium chloride from *p*-chloroaniline (12.7 g, 0.10 mol), sodium nitrite (6.9 g, 0.10 mol), and 12 *M* hydrochloric acid (50 mL) was added to a stirred ice-cold solution (300 mL) containing 1,2-diacetylhydrazine (11.6 g, 0.10 mol) and sodium carbonate (50 g), covered with diethyl ether (100 mL); it efficiently removes colored impurities and dissolves very little of the product at this temperature). There was rapid separation of **3** as the colorless crystalline hydrate. Stirring was continued for 15 min, the whole was filtered, the product washed with water and dried, finally, in a vacuum desiccator over phosphorus pentoxide; ^1H nmr analysis showed it to be the monohydrate (16 g, 65%).

A purified sample of **3** could not be obtained crystalline and free of solvent. In solvents not rigorously dried it formed the hydrate, and from anhydrous solvents containing ether the solid obtained showed ether in its ^1H nmr spectrum. Prolonged evacuation was without effect on the bound solvents. Solutions of **3** could be dried with magnesium perchlorate and gave water-free spectra, but evaporation of such solutions gave a gummy residue.

It was best recrystallized from undried chloroform-pentane as the monohydrate, which melted with decomposition at 90° ; $\nu(\text{anhydrous } \text{CHCl}_3)$: 3405 (NH), 1720 (C=O) cm^{-1} ; ^1H nmr (CDCl_3) δ : 8.05 (1H, s, NH), 7.3-7.6 (4H, m, ClC_6H_4), 2.60 (3H, s, N(3)-COCH₃), 2.17 (3H, s, N(4)-COCH₃); ^{13}C nmr (CDCl_3) δ : 170.4, 168.4 (C=O), 146.1 (C1), 135.7 (C4), 129.4 (C3), 123.8 (C2), 22.0 (CH₃), 20.5 (CH₃). *Anal.* calcd. for $\text{C}_8\text{H}_9\text{ClN}_4\text{O}_2$:

H_2O : C 44.05, H 4.80, N 20.54; found: C 43.92, H 4.78, N 20.49%.

p-Chlorobiphenyl was prepared from *p*-chloroaniline by the Gomberg-Hey reaction (28). *p*-Bromo-*p*'-chlorobiphenyl was obtained by bromination of *p*-chlorobiphenyl in acetic acid, and *p,p*'-dichlorobiphenyl by chlorination of biphenyl in acetic acid (29); *p,p*'-dibromobiphenyl was obtained in an analogous manner (30).

1-Acetyl-2-*p*-chlorophenylhydrazine (**15**) was made from *p*-chlorophenylhydrazine and one equivalent of acetic anhydride.

Gas-liquid chromatographic analyses

Biphenyl was used as an internal standard for all glc analyses.

In the case of the *p,p*'-dihalogenated biphenyls the linearity of response (signal area) over a 10-fold range of concentrations (10^{-3} - 10^{-2} *M*, greater than that encountered in the experimental work) was established; the standard deviation for six trials was 1.6%. It is known that for halogenated biphenyls the FID response shows almost no variation between different isomers (31). Thus the calibration for all isomers was based on results from standard solutions of the *p,p*'-isomer and biphenyl.

1,2-Diacetylhydrazine gave a nonlinear FID response especially at very low concentrations. A calibration curve was determined using ten standard solutions spanning the concentration range of interest. In most of the decomposition reactions the diacetylhydrazine separated out of the solution. Addition of methanol to give a homogeneous solution was necessary before the glc determination was carried out. The yield of diacetylhydrazine was not determined in all reactions.

For the determination of 1-acetyl-1-*p*-chlorophenylhydrazine (**9**) the isomeric 1-acetyl-2-*p*-chlorophenylhydrazine (**13**) was used. It was assumed they would have the same FID response.

Determination of half-life of **1**

A solution of **1** and dimethyl phthalate (as internal standard) (0.26 *M* each) in benzene in an nmr tube was immersed in refluxing benzene and the proton spectrum run at intervals. A first order plot became nonlinear after a few hours, showing that the reaction was accelerating. The half-life was about 6.4 h.

In refluxing chlorobenzene the half-life was less than 5 min.

The half-life of **3** in refluxing benzene could not be readily determined since evolution of nitrogen began almost immediately on warming.

Thermolyses

The thermal decompositions in solution were carried out using 20 mL of ca. 0.025 *M* solutions of **1**, **2**, or **3**, at suitable temperatures: benzene 80°C , chlorobenzene, bromobenzene, iodobenzene, 131°C ; anisole, 100°C ; biphenyl, 190°C ; 2-propanol, 83°C . The reactions were followed by observing the disappearance of the acetyl methyl singlets in the ^1H nmr spectrum.

Where yields were determined a known weight of biphenyl was added to the solution after completion of the reaction.

In the case of the reaction of **1** with benzene and chlorobenzene the final solutions were evaporated and the hexane-soluble portions of the residue worked up to give *p*-chlorobiphenyl and *p,p*'-dichlorobiphenyl. These were crystallized from methanol and identified by mixture mp.

Photolyses

Irradiation by a 100 or a 450 W Hanovia medium pressure mercury immersion lamp was used through quartz walls.

Routinely solutions 0.026 *M* (reactor volume 250 mL) in **1** or **3** were photolyzed (450 W) at a temperature of about 10°C . Samples were periodically removed and monitored in the aliphatic region by ^1H nmr spectroscopy. The complete decomposition required about 6 h for **1** and 2 h for **3**.

Work-up of products of photolysis of 1 in benzene

The photolysate from complete reaction of **1** (2.0 g) in benzene (250 mL) was evaporated to dryness and the residue extracted with refluxing pentane (2 × 100 mL). The pentane solution afforded 1.0 g (52%) of almost pure *p*-chlorobiphenyl; recrystallized from methanol it had mp and mixture mp 144–145°C. The pentane-insoluble fraction was then extracted with refluxing ether (2 × 100 mL) which yielded a residue (0.72 g) which had both aromatic and methyl (several peaks) absorption in its ¹H nmr spectrum. A major component was **9** (δ 2.0), which was established by gc–ms evidence, as described later. The pentane- and ether-insoluble residue contained diacetylhydrazine, which was isolated as the insoluble product obtained on addition of chloroform.

Detection of 3 as intermediate in photolysis of 1

A total of 4 mL of a solution of **1** (0.15 M) in benzene was divided among seven 5-mm nmr tubes arrayed around the 100 W lamp. Photolysis was carried out and the proton spectrum was periodically checked using different tubes randomly. After 1 1/2 hours the balance between **3** and accumulating by-products was judged to be optimal and the reaction was stopped. The combined solutions were set aside whereupon crystallization of a small amount of material soon occurred. The ¹H nmr spectrum of the crystals showed them to consist of the tetrazene **3** (δ(Me) 2.60 and 2.17, and the characteristic water peak at ca. 2.7) contaminated by a small amount of diacetylhydrazine.

Kinetic analysis of photolysis of 1 in benzene (see Table 3)

A 5-mm nmr tube containing a solution of **1** (0.26 M) in benzene was irradiated by the 100 W lamp as described above. Integration at suitable intervals of the methyl region of the proton spectrum enabled the proportions of **1**, **3**, and all other methyl-containing products to be determined. After the midpoint of the reaction separation of solid precluded further analysis.

The experiment was repeated at half the concentration (0.13 M). In this case the solution remained clear till after 80% of the reaction was complete. As expected this reaction was much slower, but the relative proportions of products were essentially unchanged.

The estimated error in the analysis was about ± 3%.

Effect of additives or catalysts on 1

In the decomposition of **1** in bromobenzene the following variations were carried out (substrate concentration as before): (i) 0.67 mol of *m*-dinitrobenzene included; (ii) solvent first degassed by refluxing, then N₂ atmosphere maintained during reaction; (iii) O₂ passed through solution during reaction.

In the anisole reaction the decomposition was carried out both without catalyst and with 3 mol of AlCl₃.

Azodiacetyl trapping experiments

(i) A solution of **1** in chlorobenzene was heated in the usual manner (131°C) except that cyclopentadiene (10 mL) was added dropwise with stirring during the course of the reaction. The glc analysis failed to detect the presence of either of the adducts **7** or **8** (17).

(ii) The experiment was repeated using refluxing 2-propanol as solvent. Both adducts **7** and **8** were observed in the glc, their identity being confirmed by coinjection with authentic samples of the adducts.

Identification of 1-acetyl-1-*p*-chlorophenylhydrazine (9)

Refluxing of *p*-chlorophenylhydrazine with ethyl formate for 30 min gave the 2-formyl derivative (70%), mp 185.5–186.5°C (lit. (32) mp 186–187°C).

The formyl derivative (0.10 g) was heated with acetic anhydride (1 mL) for 1 hour. Evaporation and examination of the

residue by ¹H nmr spectroscopy showed it consisted of a mixture of products. The mixture was hydrolyzed by heating it in 1 N H₂SO₄ (25 mL) for 15 min at 100°C, neutralized with Na₂CO₃, and extracted with ether. Gas-liquid chromatography of the extract showed a mixture having one peak with the same retention time as the major, otherwise unidentified, product obtained in the thermolysis and photolysis reactions; coinjection with a worked-up sample rich in this product (from a photolysis reaction as described above) gave a single peak. The retention time was longer than that of synthetic 1-acetyl-2-*p*-chlorophenylhydrazine.

The enriched sample was also subjected to gc–ms analysis which showed the product to have a parent peak at *m/e* 184 (³⁵Cl), one chlorophenyl ring (isotope ratio), and an acetyl group (strong peak at *m/e* 142). In the mass spectrum of the pyrolysate from the sand reaction, the peak at *m/e* 184 was the most intense. The combination of glc and ms evidence thus establishes the product as **9**.

Decompositions without solvent

(i) Gas-liquid chromatographic injection

A 3 μL sample of a solution of **1** (0.025 M) in ether containing biphenyl as internal standard was introduced into the injection port (250°C) of the gas chromatograph; the chromatogram was run under the usual operating conditions.

(ii) Pyrolysis on sand

Clean sand (20 g) was added to a solution of **1** (0.50 g, 1.27 mmol) in dichloromethane (20 mL) and the solvent removed on a rotary evaporator. The coated sand was then heated at 150°C under a Dry-Ice condenser until the reaction was judged to be complete (15 min, by which time the surface of the sand was very discolored). The product was extracted with ether, and the solution and ethereal washings from the condenser combined. Internal standard was added and the solution analyzed in the usual way.

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