Measurements. Fast kinetic measurements were carried out with a Durrum stopped-flow spectrophotometer equipped with a thermostated cell compartment (25 ± 0.2 °C). Slow rates were measured with a conventional UV–vis Kontron Uvikon spectrophotometer. All rates were reproducible to within ±3% or better. pH Determinations in water–Me_2SO mixtures containing 0.5 M NMe_4Cl were carried out at 25 °C using the same procedure as that previously described.[20] A Tacussel Isis 20000 electron pH meter was used for this purpose. The autoprotolysis constants of the 50% H_2O–50% Me_2SO–0.5 M NMe_4Cl and 20% H_2O–80% Me_2SO–0.5 M NMe_4Cl mixtures were known from previous studies: pK_s = 15.83 and 20.17 in 50% and 80% Me_2SO, respectively, at 25 °C.[1,16,20]

Acknowledgment. We are grateful to Professeur C. F. Bernasconi for helpful suggestions during the preparation of this article.

Registry No. **1a**, 3626-18-4; **1b**, 80134-75-4; **1c**, 132283-06-8; **1d**, 603-49-6; aminoacetonitrile, 540-61-4; glycine ethyl ester, 459-73-4; glycinamide, 598-41-4; 2-methoxyethylamine, 109-85-3; *n*-butylamine, 109-73-9; morpholine, 110-91-8; piperidine, 110-89-4; 2-cyanophenoxide ion, 72332-14-0; 4-cyanophenoxide ion, 14609-76-8; 2-bromophenoxide ion, 1121-17-1; 4-chlorophenoxide ion, 24573-38-4; phenoxide ion, 3229-70-7.

Supplementary Material Available: Kinetic data in the form of Tables S1–S2 (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Polar Effects in Reactions of Carbon-Centered Radicals with Diazonium Salts: Free-Radical Diazocoupling

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Carbon-centered radicals react with diazonium salts by addition, leading under reductive conditions to azo derivatives (free-radical diazocoupling), or by electron-transfer in chain processes. The reaction is highly sensitive to polar effects and it has been investigated by three different processes: (i) alkyl radicals, generated from alkyl iodides, H_2O_2, Fe(II) salt, and DMSO, have been utilized to develop a new general synthesis of alkylarylazo compounds; (ii) the reaction of aryl radicals with diazonium salts in the presence of Ti(III) or Fe(II) salts has been investigated, also in relation to the fact that the reaction products (azoarenes and biaryls) are often detected as side products in classical organic reactions of diazonium salts, catalyzed by Cu(I) salts, such as the Sandmeyer, Meerwein, and Pschorr reactions; (iii) adducts from addition of aryl radicals to vinyl acetate or vinyl ether react with diazonium salts either by diazocoupling reaction or by electron-transfer; a general synthesis of [α-(acyloxy)alkyl]arylazo compounds has been developed.

Polar effects in free-radical reactions are particularly marked when charged species are involved; in these cases, highly selective syntheses can be achieved.[1] In this account we report new syntheses of azo compounds by reductive addition of carbon-centered radicals to diazonium salts; the role of polar effects in such reactions is discussed.

Results

(i) Diazocoupling of Diazonium Salts by Alkyl Iodides, H_2O_2, Fe(II) Salts, and DMSO. A new reaction leading to alkylarylazo compounds has been developed according to eq 1

$$ArN_2^+ + RI + MeSOMe + H_2O_2 + 2Fe^{2+} \rightarrow ArN{=}NR + MeI + MeSO_2H + 2Fe^{3+} + OH^- \quad (1)$$

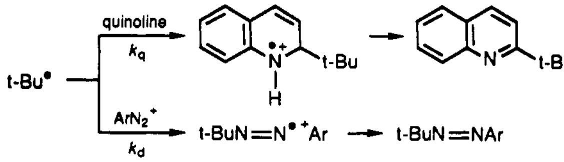
The reaction was carried out in DMSO at 0–5 °C; it proved suitable for primary, secondary and tertiary alkyl iodides, as shown by the results reported in Table I, while the presence of electron-withdrawing groups in the α-position on the alkyl iodide (e.g. ICH_2COOR, ICH_2COCH_3, ICH_2CN, $ICH(COOR)_2$, etc.) prevents the formation of the azo compound.

A competitive experiment, performed in the presence of protonated quinoline (Scheme I) allowed us to evaluate the rate constant for the addition of the *tert*-butyl radical to the diazonium salt.

Table I. Formation of RN=NAr According to eq 1

Ar	R	procedure	yield, %
Ph	t-Bu	A	68
Ph	t-Bu	B	62
Ph	i-Pr	A	51
Ph	i-Pr	C	65
Ph	i-Bu	C	61
p-ClPh	t-Bu	A	70
p-ClPh	t-Bu	B	63
p-ClPh	cyclohexyl	A	56
p-ClPh	i-Pr	C	66
p-MePh	t-Bu	B	63
p-MePh	cyclohexyl	C	62
p-MePh	i-Pr	A	52
p-MeOPh	t-Bu	A	54
p-MeOPh	cyclohexyl	A	46
o-ClPh	t-Bu	A	72
o-ClPh	cyclohexyl	C	64
o-ClPh	i-Pr	C	66
o-ClPh	n-Bu	C	36

Scheme I



The *p*-chlorobenzenediazonium salt proved to be 12.2 times more reactive than protonated quinoline toward the *tert*-butyl radical, and from the known value of k_q (4.1 ×

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[1] Minisci, F. *Substituent Effects in Radical Chemistry*; Viehe, H. G., Ed.; D. Reidel: Dordrecht, 1986; pp 391–433.

[2] Citterio, A.; Minisci, F.; Franchi, F. *J. Org. Chem.* 1980, *45*, 4752.

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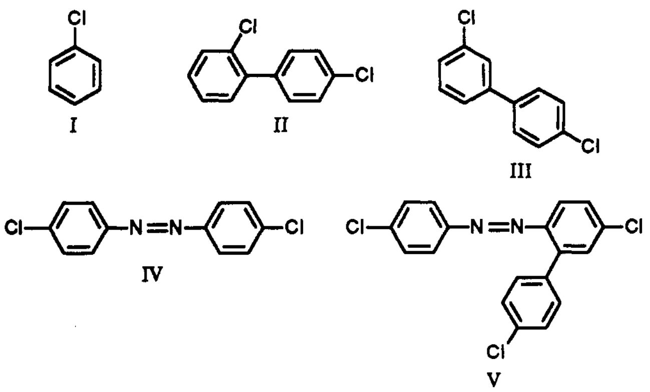
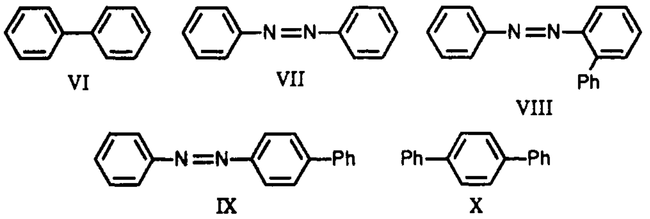
Scheme II



Scheme III



10^6 mol^{-1} s^{-1}), a value of 5×10^7 mol^{-1} s^{-1} has been estimated for k_d at 5 °C.

(ii) Reaction of Aryl Radicals with Diazonium Salts. The reduction of *p*-chlorobenzene and benzenediazonium salts by Ti(III) respectively provided compounds I–V (Scheme II) and VI–X (Scheme III) in ratios largely dependent on the reaction conditions; the azo compounds prevail in aqueous medium, whereas in the presence of organic solvents the amounts of products I, II, III, and VI increased. GLC–MS analyses excluded the presence of 4,4′-dichlorobiphenyl (XI). Compounds II, III, and XI were prepared by a simplified procedure for homolytic arylation of chlorobenzene by *p*-chloroaniline; the isomer distribution (63% ortho, 21% meta, 16% para) is identical to that previously[3] reported, obtained by a classical homolytic aromatic arylation.

Attempts of phenylation on IV by benzenediazonium salt and of *p*-chlorophenylation of VII by *p*-chlorobenzenediazonium salt failed in aqueous medium (the azoarenes were recovered unchanged); this was not surprising considering the low solubility of the azoarenes in water. On the other hand, the homolytic phenylation of azobenzene under different, known[4] conditions led to all three isomers (ortho, meta, and para), whereas the meta isomer is absent among the products reported in Scheme III. Products V, VIII, and IX, therefore, cannot arise from further arylation of IV and VII.

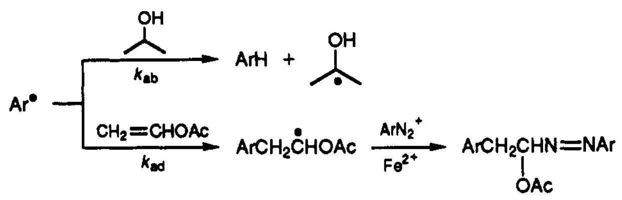
(iii) Reaction of Diazonium Salts with Vinyl Acetate and Ethyl Vinyl Ether. A new reaction, leading to [α-(acyloxy)alkyl]arylazo compounds has been developed according to eq 2. The results with benzenediazonium

$$2ArN_2^+ + CH_2{=}CHOAc + 2Fe^{2+} \rightarrow ArCH_2CH(OAc)N{=}NAr + N_2 + 2Fe^{3+} \quad (2)$$

salt, *p*-chloro- and *p*-methyl-substituted derivatives, are reported in Table IV.

A competitive experiment in the presence of 2-propanol allowed us to evaluate the rate constant of the addition of aryl radical to vinyl acetate (Scheme IV).

Scheme IV



Vinyl acetate was 2.7 times more reactive than 2-propanol toward the *p*-chlorophenyl radical, and from the known[5] value of k_{ab} (10^6 M^{-1} s^{-1}), a value of 2.7×10^6 M^{-1} s^{-1} has been estimated for k_{ad}, which has the same order of magnitude of the rate determined for the addition of aryl radical to diazonium salts, so that an excess of vinyl acetate has to be used in order to achieve a selective process. With *p*-cyanobenzenediazonium salt, under the same conditions, the reaction has a quite different behavior: *p*-cyanophenylacetaldehyde was obtained in 60% yield (eq 3), and no azo compound was formed.

$$p\text{-}CNPhN_2^+ + CH_2{=}CHOAc + H_2O \rightarrow p\text{-}CNPhCH_2CHO + N_2 + AcOH + H^+ \quad (3)$$

Phenylacetaldehyde was formed in 65% yield, without any trace of azo compounds, by using ethyl vinyl ether instead of vinyl acetate with benzenediazonium salt (eq 4).

$$PhN_2^+ + CH_2{=}CHOEt + H_2O \rightarrow PhCH_2CHO + N_2 + EtOH + H^+ \quad (4)$$

Discussion

The mechanisms of the new reactions reported in i–iii have as a common feature the interaction of carbon-centered radicals with diazonium salts.

(i) A complex, but selective, process is involved in eq 1; the redox decomposition of H_2O_2 in DMSO generates a methyl radical,[6] which then reacts with alkyl iodides;[7] the equilibrium is shifted to the right because it is governed by the enthalpic effect; the selectivity would appear to be determined by an addition–elimination mechanism[8] (eq 5).

$$Me^\bullet + RI \rightleftarrows Me\dot{I}R \rightleftarrows MeI + R^\bullet \quad (5)$$

The reactivity of alkyl radicals toward diazonium salts is governed by the polar effects (eq 6); any alkyl radical not bearing an electron-withdrawing group close to the radical center is more nucleophilic than the methyl radical and will therefore add more quickly to the diazonium salt than does the methyl radical.

$$R^\bullet + \overset{+}{N}{\equiv}NAr \rightarrow [R^+\ {}^\bullet N{=}NAr]^\bullet \rightarrow RN{=}\overset{+\bullet}{N}Ar \quad (6)$$

Reduction of the radical adducts by Fe(II) salt leads to the alkylarylazo compound (eq 7).

$$RN{=}\overset{+\bullet}{N}Ar + Fe^{2+} \rightarrow RN{=}NAr + Fe^{3+} \quad (7)$$

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[3] Ito, R.; Migita, T.; Morikawa, N.; Simamura, O. *Tetrahedron* **1965**, *21*, 955.

[4] Miller, J.; Paul, D. B.; Wong, L. V.; Kelso, A. G. *J. Chem. Soc. B* **1970**, 62.

[5] Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.

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[7] Hawari, J. A.; Kanabus-Kaminska, J. M.; Wayner, D. D. M.; Griller, D. ref 1, p 81.

[8] This mechanism has been suggested by D. H. R. Barton (personal suggestion); K. U. Ingold seems to have obtained preliminary spectroscopic evidence concerning the intermediate radical adduct (personal communication).

Table II. Products of the Reaction between the *p*-Chlorophenyl Radical and *p*-Chlorobenzenediazonium Salt

			ratios of the products I–V				
solvent	diazonium salt	Ti(III)	I	II	III	IV	V
H_2O	sulfate	chloride	traces	0.4	5.0	9.6	52.0
H_2O/MeOH (1:2)	sulfate	chloride	7.1	4.5	49.3	8.3	11.0
H_2O/i-PrOH (1:2)	sulfate	chloride	13.0	4.2	47.5	7.2	9.8
H_2O/i-PrOH (1:4)	sulfate	chloride	42.5	3.7	33.9	4.5	4.2
H_2O/i-PrOH (1:8)	sulfate	chloride	75.0	1.2	12.0	2.0	
i-PrOH	fluoborate	chloride	100				
DMSO	fluoborate	chloride	100				
CH_3CN	fluoborate	sulfate	5.8	0.7	6.5	5.3	63.5
CH_3CN[a]	fluoborate	sulfate	29.0	2.9	31.0	11.5	13.0

[a] The reaction was carried out in the presence of $CuSO_4$.

Table III. Products of the Reaction between the Phenyl Radical and Benzenediazonium Salt[a]

solvent	diazonium salt	biphenyl	VII	VIII	IX	X
H_2O	sulfate	1	30.4	7.0	22.0	traces
H_2O/MeOH (1:2)	sulfate	58	21	1	3	4
CH_3CN	fluoborate	7.2	29.6	6.1	19.4	pl

[a] Benzene was formed in the presence of MeOH and in acetonitrile, but it was not quantitatively evaluated.

Table IV. Formation $ArCH_2CH(OAc)N{=}NAr$ According to eqs 12–15

Ar	procedure	yield, %
Ph	A	87.9
p-MePh	A	89.1
p-ClPh	A	80.5
p-ClPh	B	65.0

The importance of the polar effect is emphasized by the high rate constant (5×10^7 M^{-1} s^{-1}) for the addition of the *tert*-butyl radical to the diazonium group. Moreover, no reaction occurs between diazonium salts and alkyl radicals bearing electron-withdrawing groups in the α-position, which, on the opposite, smoothly react with electron-rich aromatics and alkenes[9] under the same reaction conditions, thus emphasizing the fundamental role of the polar effect.

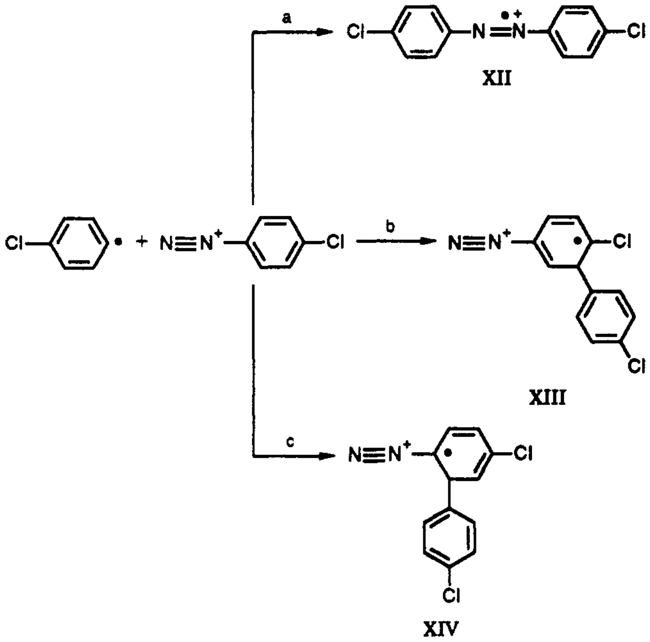
The same radical source has been recently utilized for homolytic alkylation on heteroaromatic bases[10] and quinones[11] by nucleophilic alkyl radicals and on electron-rich aromatics and alkenes[9] by electrophilic alkyl radicals.

(ii) The results reported in Table II show for the first time, at least to our knowledge, that the redox decomposition of para-substituted diazonium salts leads to the 3,4′-biaryl, with minor amount of the 2,4′-isomer and no 4,4′-isomer, which is the only one previously[12] reported for the copper-catalyzed reactions. The mechanism we suggest for the formation of compounds I–X involves the initial formation of an aryl radical by redox decomposition of the diazonium salt (eq 8) and its subsequent interaction with either the solvent or the diazonium salt.

$$Ti^{3+} + \overset{+}{N}{\equiv}NAr \rightarrow Ti^{4+} + {}^{\bullet}N{=}NAr \rightarrow Ar^{\bullet} + N_2 \qquad (8)$$

Hydrogen abstraction from the solvent leads to I through a chain process. This is clearly shown in Table II by the increasing formation of chlorobenzene as the amount of 2-propanol in the solvent is increased. To rationalize the formation of compounds II–X we suggest an unselective interaction of the aryl radical with the undecomposed diazonium salt (Scheme V).

Scheme V

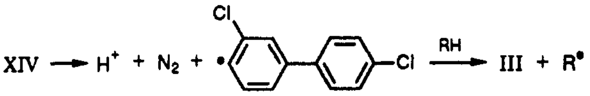


Route a leads to IV by reduction of XII (eq 9).

$$p\text{-}ClC_6H_4N{=}N^{\bullet+}C_6H_4Cl\text{-}p + Ti^{3+} \rightarrow p\text{-}ClC_6H_4N{=}NC_6H_4Cl\text{-}p + Ti^{4+} \qquad (9)$$

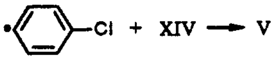
XIII and XIV respectively lead to dichlorobiphenyls II and III, either by reduction (eq 10) or by hydrogen abstraction by the corresponding biphenyl radicals (eq 11).

$$XIV + Ti^{3+} \rightarrow III + Ti^{4+} + N_2 \qquad (10)$$



(11)

XIV is a stabilized cyclohexadienyl radical, and it likely has some persistency, which allows to reach a stationary concentration, suitable for acting as a trap of the *p*-chlorophenyl radical, leading to the formation of V (eq 12).



(12)

The formation of biphenyl and azo derivatives from ben-

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(9) Minisci, F. *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K.-D., Eds.; Plenum Press: New York, 1990, p 303.

(10) Minisci, F.; Vismara, E.; Fontana, F. *J. Org. Chem.* **1989**, *54*, 5224.

(11) Coppa, F.; Fontana, F.; Minisci, F.; Nogueira Barbosa, M. C.; Vismara, E. *Tetrahedron* **1991**, *47*, 7343.

(12) Hegarty, A. F. *The Chemistry of the Diazonium Group*; Patai, S., Ed.; Wiley: New York, 1978; p 556.

zenediazonium salts can be explained in a similar way. The results in Table II also allow us to evaluate the order of magnitude of the rate constant for the addition of aryl radical to the diazonium group ($\sim 10^6$ M^{-1} s^{-1}), since the rate of hydrogen abstraction from 2-propanol by aryl radicals is known;[5] it is at least 1 order of magnitude lower compared to the same reaction of the *tert*-butyl radical. Thus, aryl radicals are generally much more reactive and less selective than alkyl radicals for enthalpic reasons, and their reactivity is poorly affected by polar effects,[13] whose presence reverses the reactivity–selectivity principle: in fact, the *tert*-butyl radical, due to polar effects, is more reactive than aryl radicals toward the diazonium group, but it is also much more selective. This behavior is quite similar to that observed between alkyl and aryl radicals with protonated heteroaromatic bases.[13]

(iii) As far as we know, reaction 2 is the only synthetic approach to the class of [α-(acyloxy)alkyl]arylazo compounds. The mechanism of this reaction involves reduction of the diazonium salt by Fe(II) (eq 13). Addition of

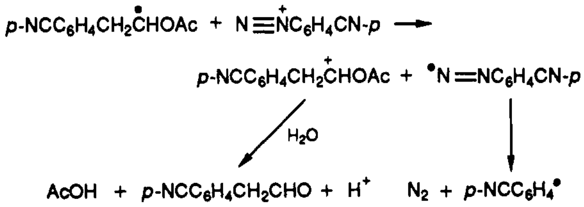
$$Fe^{2+} + Ar\overset{+}{N}{\equiv}N \rightarrow Fe^{3+} + ArN{=}N^{\bullet} \rightarrow Ar^{\bullet} + N_2 \qquad (13)$$

the aryl radical to vinyl acetate (eq 14) and diazocoupling of the radical adduct (eqs 15 and 16) lead to the azo compound. With *p*-cyanobenzenediazonium salt an electron-transfer chain process occurs (eq 17). Electron transfer in a chain process occurs in any case with vinyl ether (eq 18). Thus, small structural changes either in the diazonium salt (increasing of the redox potential by cyano group) or in the vinyl radical adduct (decreasing of the redox potential by the alkoxy group) dramatically shifts the reaction course from diazocoupling (eq 15) to electron transfer (eqs 17 and 18).

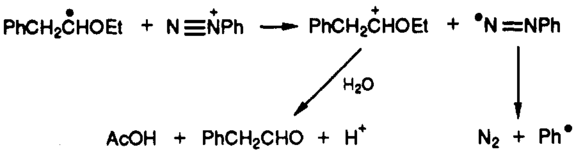
$$Ar^{\bullet} + CH_2{=}CHOAc \rightarrow ArCH_2\dot{C}HOAc \qquad (14)$$

$$ArCH_2\dot{C}HOAc + N{\equiv}\overset{+}{N}Ar \rightarrow ArCH_2CH(OAc)N{=}\overset{+\cdot}{N}Ar \qquad (15)$$

$$ArCH_2CH(OAc)N{=}\overset{+\cdot}{N}Ar + Fe^{2+} \rightarrow ArCH_2CH(OAc)N{=}NAr + Fe^{3+} \qquad (16)$$



(17)



(18)

Conclusions

Diazocoupling of carbon-centered radicals with diazonium salts is a quite general reaction, in which polar effects play a dominant role. Four kinds of behavior have been recognized in the reaction of carbon-centered radicals with diazonium salts: (a) alkyl radicals without strongly polar substituents close to the radical center add rapidly and selectively to the diazonium group; (b) electron-withdrawing groups bonded to the radical center on alkyl radicals inhibit the reaction; (c) electron-donating groups shift the reaction of alkyl radicals toward an electron-transfer process; (d) aryl radicals, due to their low polar character, add with low selectivity to diazonium salts, attacking both the diazonium group and the benzene ring.

Experimental Section

General Procedures for Diazocoupling by Alkyl Iodides. (A) $NaNO_2$ (4.2 mmol) in 2.5 mL of water was added with stirring at 0 °C to a solution of 4 mmol of the aromatic amine in 7.5 mL of 10% H_2SO_4. $FeSO_4{\cdot}7H_2O$ (8 mmol) in 80 mL of DMSO, 10 mmol of the alkyl iodide, and 8 mmol of 30% H_2O_2 was simultaneously dropped into the resulting mixture with stirring at 0–5 °C. The solution was diluted with water and extracted with hexane. The reaction products were isolated by flash chromatography (SiO_2, 7:1 hexane–ethyl acetate) and identified by comparison with authentic samples obtained by the previously[14] developed procedure (molecular ions observed in mass spectra and UV absorption (EtOH), α_{max} 403 nm (log ϵ = 2.25) and α 264 nm (log ϵ = 4.22), indicate that the azo derivatives are not isomerized to the more stable arylhydrazones with secondary alkyl groups) and analyzed by GLC (azobenzene as internal standard) and GLC–MS.

(B) $FeSO_4{\cdot}7H_2O$ (8 mmol) in 80 mL of DMSO, 10 mmol of alkyl iodides, and 8 mmol of 30% H_2O_2 was simultaneously dropped with stirring at 0–5 °C into a solution of 4 mmol of diazonium fluoborate in 10 mL of DMSO; the resulting solution was worked up as in A.

(C) The procedure is similar to B, but the alkyl iodide is dissolved in the DMSO solution of the fluoborate; this procedure is more suitable for secondary alkyl iodides, which are more stable than tertiary alkyl iodides in DMSO. The results are reported in Table I.

Competitive Addition of t-Bu• to Protonated Quinoline and *p*-Chlorobenzenediazonium Salt. Procedure A was utilized; 12 mmol of quinoline was added to the solution of *p*-chlorobenzenediazonium salt (4 mmol). Only 2 mmol of H_2O_2 and $FeSO_4{\cdot}7H_2O$ were used in order to obtain low conversions. The reaction products were analyzed by GLC with azobenzene as internal standard; the molar ratio between 2-*tert*-butylquinoline and *tert*-butyl(*p*-chlorophenyl)azo compound was 0.246.

General Procedures for the Reaction of Aryl Radicals with Diazonium Salts. (A) A solution of 3.3 mmol of $NaNO_2$ in 2 mL of water was dropped with stirring at 0–2 °C into a solution of 3.2 mmol of *p*-chloroaniline in 6 mL of 10% H_2SO_4. The amount of solvent reported in Table II was added, and an aqueous solution (15%) of Ti(III) salt was dropped with stirring at 0–5 °C until the persistence of the violet color. The mixture was further diluted with water and extracted by CH_2Cl_2. Chlorobenzene and the dichlorobiphenyls II and III were detected by GLC and identified by comparison with authentic samples. The injection of a pure sample of 4,4′-dichlorobiphenyl in GLC as compared to the GLC analysis of the reaction mixture revealed the absence of this isomer among the reaction products. The products IV and V were isolated by column chromatography (SiO_2, hexane) and characterized as follows. IV: mp 186 °C (lit.[15] mp 186 °C); mass spectrum, *m/z* 252 (M^+), 141 ($M^+ - C_6H_4Cl$), 111 (C_6H_4Cl); NMR ($CDCl_3$) δ (ppm) 7.45 (d, 4 H), 7.86 (d, 4 H). V: mp 154 °C (lit.[16] mp 153 °C); mass spectrum, *m/z* 362 (M^+), 186 (III); NMR ($CDCl_3$) δ (ppm) 7.44 (m, 7 H), 7.55 (d, 1 H), 7.7 (m, 3 H). MS and NMR spectra are identical to those of pure samples obtained by known procedures.[15,16]

(B) The procedure is identical to A, but the diazonium fluoborate has been dissolved in the organic solvents reported in Table II.

***p*-Chlorophenylation of Chlorobenzene.** A solution of 5 g of *p*-chloroaniline and 4.5 g of CCl_3COOH in 45 mL of chlorobenzene was dropped at 85 °C during 5 h with stirring to a

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(14) Citterio, A.; Minisci, F. *J. Org. Chem.* **1982**, *47*, 1759.

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(16) Ford, M. C.; Waters, W. A.; Young, H. T. *J. Chem. Soc.* **1950**, 833.

mixture of CuCl (0.5 g) and $NaNO_2$ (2.6 g) in 30 mL of chlorobenzene. The reaction mixture was stirred for 2 more hours at 85 °C and then washed with 5% aqueous solution of HCl, aqueous $NaHCO_3$, and water. The GLC analysis of the organic solution shows the presence of 2,4′-, 3,4′-, and 4,4′-dichlorobiphenyls (respectively 63%, 21%, and 16%) in 58% overall yield; the isomer distribution is identical to that previously determined[3] by a different radical source (63.8%, 20.5%, and 15.7%, respectively). These isomers were utilized for the identification by GLC analysis of the products obtained from the redox decomposition of the *p*-chlorobenzenediazonium salt.

Benzenediazonium Salt. The same procedures utilized for the *p*-chloro derivative were used. Benzene was present among the reaction products in the organic layer, but it was not quantitatively evaluated. Biphenyl, terphenyl (X), and azobenzene were identified by comparison with pure commercial samples and analyzed by GLC. The azo derivatives VIII and IX were isolated by column chromatography (SiO_2, hexane). VIII: mp 40 °C (lit.[4] mp 38–39 °C). IX: mp 154 °C (lit.[17] mp 153–154 °C).

A mixture of *o*-, *m*-, and *p*-phenylazobenzenes was prepared by the known[4] procedure of homolytic phenylation of azobenzene; GLC and GLC–MS analysis have shown that the meta isomer is not formed during the redox decomposition of the benzenediazonium salt. The mass spectra of VIII and IX are quite similar, showing *m/z* 258 (M^+), 152, 126, and 105.

General Procedures for the Reaction of Diazonium Salts with Vinyl Acetate. (A) Solid $FeSO_4{\cdot}7H_2O$ (2 mmol) was added to 1 mmol of diazonium fluoborate in 5 mL of vinyl acetate and 5 mL of DMSO with stirring at 5 °C. The mixture was stirred during 30 min, diluted with 50 mL of water, and extracted by CH_2Cl_2. GLC analysis reveals the presence of only one reaction product, which was isolated by column chromatography (SiO_2, 8:1 hexane–ethyl acetate) and identified by MS and NMR spectra as aryl(α-acetoxy-β-arylethyl)azo compound. The results are reported in Table IV.

From benzenediazonium fluoborate: pale yellow oil; mass spectrum, *m/z* 268 (M^+), main fragments 163 ($PhCH_2CHOAc$), 105 (PhN=N); NMR ($CDCl_3$) δ (ppm) 2.12 (s, 3 H, CH_3COO), 3.21 (m, 2 H, CH_2), 6.30 (q, 1 H, CH), 7 aromatic H, m centered at 7.15, 3 aromatic H, m centered at 7.58 ppm.

From *p*-methylbenzenediazonium fluoborate: pale yellow oil; mass spectrum, *m/z* 296 (M^+), main fragments 177 ($MeC_6H_4CH_2CHOAc$) and 119 ($MeC_6H_4N{=}N$); NMR ($CDCl_3$) δ (ppm) 2.13 (s, 3 H, CH_3COO), 2.30 (s, 3 H, CH_3PhC), 2.39 (s, 3 H, $CH_3C_6H_4N{=}N$), 3.22 (m, 2 H, CH_2), 6.31 (q, 1 H, CH), 6 aromatic H, m centered at 7.12, 2 aromatic H, d centered at 7.60.

From *p*-chlorobenzenediazonium fluoborate: pale yellow oil; mass spectrum, *m/z* 337 (M^+), main fragments 197 (ClC_6H_4CHOAc) and 139 ($ClC_6H_4N{=}N$), NMR ($CDCl_3$) δ (ppm) 2.12 (s, 3 H, CH_3COO), 3.20 (m, 2 H, CH_2), 6.32 (q, 1 H, CH), 4 aromatic H, m centered at 7.20, 2 aromatic H, m centered at 7.65.

(B) A solution of 5.2 mmol of $NaNO_2$ in 4 mL of water was dropped with stirring at 0–3 °C into a solution of 5 mmol of aromatic amine in 15 mL of 10% H_2SO_4. This mixture was diluted with 10 mL of vinyl acetate and 15 mL of DMSO, and then 10 mmol of solid $FeSO_4{\cdot}7H_2O$ was added with stirring at 5 °C. The resulting mixture was then worked up as in procedure A.

Reaction of *p*-Cyanobenzenediazonium Salt with Vinyl Acetate. Procedure B was utilized. GLC and GLC–MS analyses reveal the presence of *p*-cyanophenylacetaldehyde in 60% yield, but no trace of the [α-(acyloxy)alkyl]arylazo compound: mass spectrum of *p*-cyanophenylacetaldehyde *m/z* 145 (M^+), 116 (M^+ – CHO), 90 (116 – CN); IR (neat) 2215 (C≡N stretching), 1728 (CHO) cm^{-1}.

Competitive Reaction of the *p*-Chlorophenyl Radical with 2-Propanol and Vinyl Acetate. Procedure A was utilized, by using equimolecular amounts of vinyl acetate and 2-propanol. Chlorobenzene and *p*-chlorophenyl[α-acetoxy-β-(*p*-chlorophenyl)ethyl]azo compound were analyzed by GLC (azobenzene as internal standard); the molar ratio was 0.37.

Reaction of Benzenediazonium Salt with Ethyl Vinyl Ether. (A) Procedure A utilizing vinyl acetate was used; a fast reaction took place after addition of a catalytic amount of $FeSO_4{\cdot}7H_2O$ (0.1 mmol) and was completed in a few minutes. The reaction mixture, diluted with water and extracted with CH_2Cl_2, provided phenylacetaldehyde, identified by comparison with a commercial sample, in 65% yield, while GLC–MS did not reveal traces of phenyl(α-ethoxy-β-phenylethyl)azo compound.

(B) $TiCl_3$ (0.5 mmol; 15% aqueous solution) was dropped into a solution of 1 mmol of diazonium fluoborate in 5 mL of ethyl vinyl ether and 15 mL of acetonitrile with stirring at 0–5 °C. A fast reaction took place, which was completed in a few minutes. The solution was then diluted with 50 mL of water, extracted with CH_2Cl_2, and analyzed as in A; phenylacetaldehyde was obtained in 45% yield, and no (α-ethoxyalkyl)arylazo compound was detected by GLC–MS analysis.

Registry No. IV, 1602-00-2; V, 141320-17-4; VIII, 14336-17-5; IX, 7466-42-4; $PhN_2^+{\cdot}HBF_3^-$, 141320-21-0; *p*-$ClPhN_2^+{\cdot}HBF_3^-$, 141344-01-6; *p*-$MeOPhN_2^+{\cdot}HBF_3^-$, 141344-02-7; *p*-$MePhN_2^+{\cdot}HBF_3^-$, 141320-22-1; *o*-$ClPhN_2^+{\cdot}HBF_3^-$, 141320-23-2; *t*-BuI, 558-17-8; *i*-PrI, 75-30-9; *i*-BuI, 513-38-2; c-$C_6H_{11}I$, 626-62-0; PhN=NBu-*t*, 1775-83-3; PhN=NPr-*i*, 1075-73-6; PhN=NBu-*i*, 84113-61-1; *p*-ClPhN=NBu-*t*, 80228-01-9; *p*-ClPhN=N-c-C_6H_{11}, 80228-00-8; *p*-ClPhN=NPr-*i*, 80228-03-1; *p*-MePhN=NBu-*t*, 131457-28-8; *p*-MePhN=N-c-C_6H_{11}, 141320-11-8; *p*-MePhN=NPr-*i*, 141320-12-9; *p*-MeOPhN=NBu-*t*, 131457-29-9; *p*-MeOPhN=N-c-C_6H_{11}, 141320-13-0; *o*-ClPhN=NBu-*t*, 136412-81-2; *o*-ClPhN=N-c-C_6H_{11}, 141320-14-1; *o*-ClPhN=NPr-*i*, 141320-15-2; *o*-ClPhN=NBu-*n*, 141320-16-3; *n*-BuI, 542-69-8; $PhNH_2$, 62-53-3; *p*-$ClPhNH_2$, 106-47-8; *p*-$MePhNH_2$, 106-49-0; *p*-$MeOPhNH_2$, 104-94-9; *o*-$ClPhNH_2$, 95-51-2; $PhCH_2CH(OAc)$-N=NPh, 141320-19-6; *p*-$MePhCH_2CH(OAc)N{=}N$-*p*-PhMe, 141320-20-9; *p*-$ClPhCH_2CH(OAc)N{=}N$-*p*-PhCl, 141344-00-5; *p*-$CNPhNH_2$, 873-74-5; chlorobenzene, 108-90-7; vinyl acetate, 108-05-4; *p*-cyanophenylacetaldehyde, 76113-58-1.