Reaction of Azoarenes with Tributyltin Hydride

Angelo Alberti,† Nicola Bedogni,‡ Massimo Benaglia,† Rino Leardini,‡ Daniele Nanni,‡ Gian Franco Pedulli,‡ Antonio Tundo,‡ and Giuseppe Zanardi*,‡

I.C.O.C.E.A. C.N.R., I-40064 Ozzano Emilia, Bologna, Italy, and Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, Viale Risorgimento 4, I-40136, Bologna, Italy

Received May 28, 1991

Tributyltin hydride when reacted with a series of substituted azoarenes afforded hydrazo compounds with high chemoselectivity and good to high yields. With ortho-substituted azoarenes, mixtures of hydrazo derivatives and N-heterocycles or cyclic products only were obtained. The kinetic law of the process was determined in the presence and in the absence of AIBN; with the radical initiator the reaction proceeds via a radical chain mechanism, whereas without AIBN the presence of stannyl free radicals could be discarded. The mechanism of the noninitiated reaction is discussed. EPR characterization of spin adducts obtained by reacting group IVB organometallic radicals with azo compounds is reported.

The reducing ability of tin hydrides has been exploited with a variety of organic substrates[1] and it has been shown that these reductions usually proceed through a radical chain mechanism initiated either by a radical initiator[2] or by a single electron transfer (SET).[3] In some cases, evidence supporting an ionic mechanism (hydride transfer) has been reported.[4]

The reduction of azoarenes to the corresponding hydrazoarenes can be carried out with a variety of reducing agents under different experimental conditions.[5] Two examples of reduction by means of tin hydrides have also been reported, namely, those of azobenzene and of dialkyl azodicarboxylates: these reactions were shown to proceed via the initial formation of a 1:1 adduct between the azo derivative and the tin hydride followed by hydrolysis to give the hydrazo compound.[6]

In order to get a better insight on the mechanism of the reduction of azoarenes with tributyltin hydride and to evaluate its synthetic potential, we have carried out a detailed investigation on the reduction of a number of different azo substrates by combining product studies with the results of kinetic and spectroscopic measurements.

Results and Discussion

By reacting azobenzene (**1a**) (0.1 M) with Bu_3SnH (0.3 M) in refluxing benzene for 3–5 h, hydrazobenzene was obtained in almost quantitative yield (eq 1) after chromatographic workup. When repeated with a number of substituted azobenzenes (**1b–o**) the reaction led again to the corresponding substituted hydrazo compounds **2** in good to high yields (see Table I). By carrying out the reactions with equimolecular amounts of the reactants, the products were the same as those obtained with an excess of tin hydride, although the reaction time increased.

$$\underset{\mathbf{1}}{ArN{=}NAr'} \xrightarrow[\text{benzene},\Delta]{Bu_3SnH} \underset{\mathbf{2}}{ArNHNHAr'} \qquad (1)$$

This synthetic method to hydrazo derivatives, at least in the above cases, provides for in high chemoselectivity a convenient route alternative to other established methods, since it does not affect other functional groups which are usually reduced by other agents. Moreover, the neutral conditions in which the reduction is carried out prevent the occurrence of the benzidinic rearrangement which may take place in acidic media.

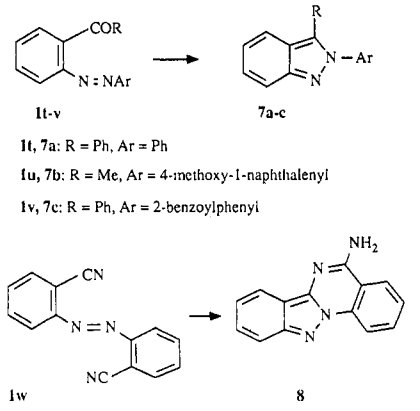
With azoarenes bearing substituents such as CN, COOR, or CH_2OH ortho to the azo function, the reduction was less selective since, besides hydrazo compounds, heterocyclic products were formed. In particular, compounds **3**, **4**, **5**, and **6** were obtained from 2-cyano- (**1p**), 2-carbomethoxy-

Table I. Yields of the Hydrazo Compounds 2a–o Obtained from the Reaction of Azoarenes 1a–o with Tributyltin Hydride in the Absence of AIBN

compd	Ar	Ar′	yield,[a] %
2a	Ph	Ph	92
2b	Ph	4-MeC_6H_4	92
2c	Ph	4-$MeOC_6H_4$	89
2d	Ph	4-ClC_6H_4	87
2e	Ph	4-BrC_6H_4	84
2f	Ph	4-IC_6H_4	87
2g	Ph	4-NCC_6H_4	91
2h	Ph	4-$MeC(O)C_6H_4$	89
2i	Ph	4-$MeOC(O)C_6H_4$	91
2j	Ph	4-$HOOCC_6H_4$	83
2k	Ph	4-$PhC(O)OC_6H_4$	86
2l	Ph	3-pyridyl	81
2m	3,5-$(MeO)_2C_6H_3$	3,5-$(MeO)_2C_6H_3$	89
2n	Ph	2-IC_6H_4	74
2o	Ph	3-IC_6H_4	87

[a] Yields are based on the total amounts of products **2** obtained by concentration and filtration of the reaction mixtures and by column chromatography of the filtrate.

Scheme I

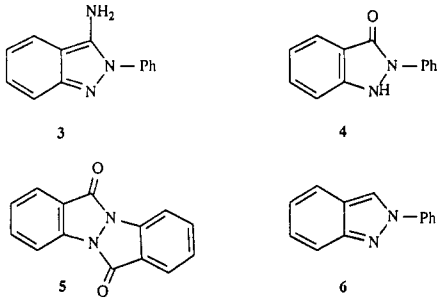


(1) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, Pergamon Press: Oxford, 1986.
(2) Neumann, W. P. *Synthesis* **1987**, 665.
(3) Tanner, D. D.; Diaz, G. E.; Potter, A. *J. Org. Chem.* **1985**, *50*, 2149.
(4) Murphy, J. A.; Sherburn, M. S.; Dickinson, J. M.; Goodman, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1069.
(5) Patai, S. *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*, Part 2; John Wiley and Sons: London, 1975; p 604.
(6) Noltes, J. G. *Recl. Trav. Chim.* **1964**, *83*, 515.

† I.C.O.C.E.A. C.N.R.
‡ Università di Bologna.

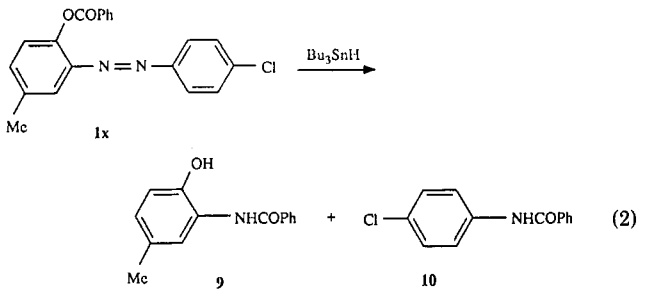
0022-3263/92/1957-0607$03.00/0

(1q), 2,2′-dicarbomethoxy- (1r), and 2-(hydroxymethyl)-azobenzene (1s), respectively.



Cyclization was the only observed reaction with the *o*-acyl-substituted azoarenes 1t–w (Scheme I).

The Bu_3SnH reduction of 2-(benzoyloxy)-5-methyl-4′-chloroazobenzene (1x) afforded instead benzanilides 9 and 10 owing to the migration of the benzoyl group and cleavage of the nitrogen–nitrogen bond (eq 2).



(2)

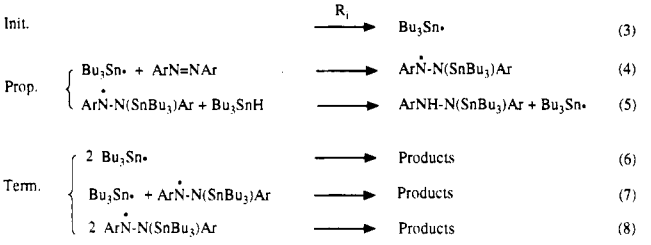
4-(Trityloxy)azobenzene (1y) and 3-(trityloxy)azobenzene (1z) behaved differently when reacted with an equimolecular amount of tin hydride, the former affording triphenylmethane and 4-hydroxyazobenzene and the latter only the corresponding hydrazo derivative.

The well-known radical chain mechanism exemplified in Scheme II can be discarded for this reaction because the three (o, m, p) iodo-substituted azo compounds 1f, 1n, and 1o (see Table I) are converted to the corresponding hydrazoarenes without loss of iodine. In fact, abstraction of iodine by stannyl radicals being a very fast process,[7] it should successfully compete with reaction 4 and eventually lead to deiodinated hydrazo derivatives. Further evidence against a radical pathway is provided by the observation that the reaction takes place even in the dark and is not inhibited by the presence of oxygen.

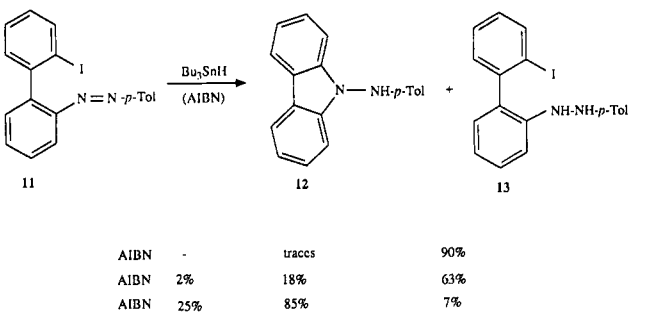
Stannyl radicals may be involved as reaction intermediates when a radical initiator such as α,α'-azobis(isobutyronitrile) (AIBN), which on its own is inert toward azo compounds, is used. As a mechanistic probe we examined the reduction of 2-iodo-2′-(4-tolylazo)biphenyl (11), since the corresponding aryl radical formed by homolysis of the iodine–aryl bond is known to attack intramolecularly the azo group, affording a cyclic hydrazyl radical.[8] When 11 (0.1 M) was refluxed in benzene with tributyltin hydride (0.3 M), the corresponding hydrazo compound 13 was exclusively obtained; in the presence of 2% AIBN, 13 was still the main reaction product, while in the presence of 25% AIBN, the carbazole 12 in 85% yield and trace amounts of the hydrazo derivative 13 were isolated (Scheme III).

Similarly, 2-iodoazobenzene (1n), when reacted in the presence of catalytic amounts of AIBN, afforded along with 2-iodohydrazobenzene (2n) small amounts of hydrazobenzene (2a), azobenzene (1a), and 2-phenylazobenzene,

Scheme II



Scheme III



AIBN	-	traces	90%
AIBN	2%	18%	63%
AIBN	25%	85%	7%

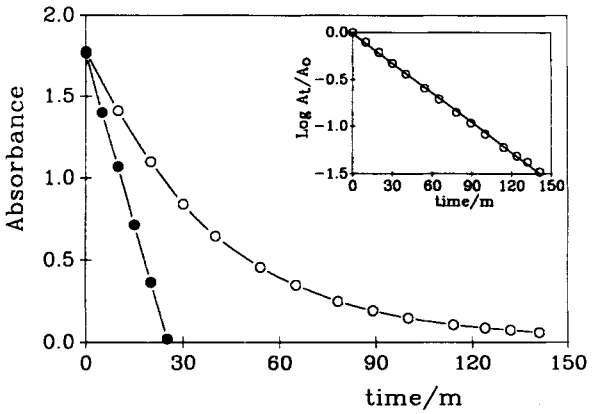


Figure 1. Decay curves at 80 °C of the absorption at 448 nm for *tert*-butylbenzene solutions of azobenzene (0.1 M) and Bu_3SnH (0.86 M) in the absence (○) and in the presence (●) of 0.1 M AIBN.

the yields of these last three products increasing with the amount of AIBN.

The different mechanisms of the spontaneous and initiated reactions between azoarenes and tin hydride were also demonstrated by kinetic studies. These were carried out by spectrophotometrically monitoring the disappearance of the red color (λ_{max} = 448 nm) of azobenzene in the presence of variable amounts of Bu_3SnH. The experimental curves fitted a good pseudo-first-order decay (see Figure 1) for concentrations of Bu_3SnH largely exceeding that of azobenzene, with measured rate constants varying linearly with the hydride concentration. Second-order decay was instead found with stoichiometric mixtures of the tin hydride and azo compound. Thus, the kinetic equation for the disappearance of azobenzene can be written as

$$-d[PhN{=}NPh]/dt = k_{exp}[Bu_3SnH][PhN{=}NPh] \quad (9)$$

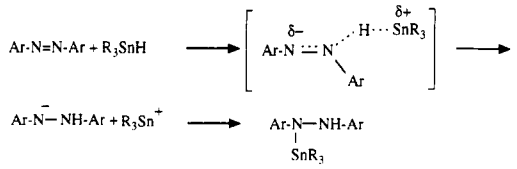
with $k_{exp} = 4.25 \times 10^{-4}$ M^{-1} s^{-1} at 80 °C.

The activation parameters for the reaction were also determined as E_a = 17.6 ± 0.4 kcal/mol, log (A/M^{-1} s^{-1}) = 7.5 ± 0.3, by running kinetic experiments in the temperature range 55–80 °C in *tert*-butylbenzene.

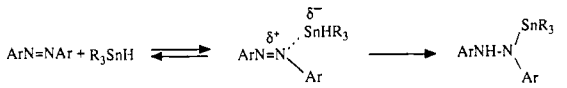
(7) Ingold, K. U.; Luzstyk, J.; Scaiano J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343.

(8) Benati, L.; Placucci, G.; Spagnolo, P.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1684.

Scheme IV



Scheme V

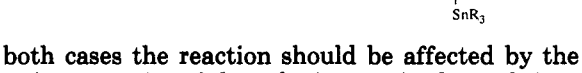


The decay of azobenzene was also followed in oxygen-saturated solutions at 80 °C; under these conditions, the rate constant for the reaction (4.15×10^{-4} M^{-1} s^{-1}) was practically identical to that measured under air or under nitrogen. Kinetic studies carried out for the reaction of 4-cyano- (**1g**) and 4-methoxyazobenzene (**1c**) with Bu_3SnH showed that the rate constants at 80 °C, i.e., 1.43×10^{-3} and 2.22×10^{-4} M^{-1} s^{-1}, respectively, depend on the nature of the substituent, with electron-releasing groups producing a decrease and electron-withdrawing groups an increase in the reaction rate. This suggests that a transition state having some degree of polarity is involved in the reaction.

The reduction of **1a** (0.1 M) with an excess of Bu_3SnH (0.86 M) was also carried out in the presence of AIBN. When using a low concentration of AIBN (0.01 M), the reaction still followed pseudo-first-order kinetics, showing only a small increase of the rate constant, $k^{353} = 5.42 \times 10^{-4}$ M^{-1} s^{-1}. In the presence of a larger amount of AIBN (0.1 M), the decay became much faster, following zero-order kinetics with a rate of 6.6×10^{-5} M s^{-1} (Figure 1). Within the assumption that in the presence of AIBN Scheme II is operative and that the relevant termination step is the coupling of the hydrazyl radicals (eq 8), zero order in azobenzene is predicted independently of the kinetic chain length. On the other hand, if termination occurs by combination of stannyl and hydrazyl radicals (eq 7), the reaction is predicted to be half order and zero order in the concentration of **1a** for a long and a short chain length, respectively. Since the length of the radical chain, $(-d[\mathbf{1a}]/dt)/2k_i e[\text{AIBN}]$, calculated by using $k_i^{353} = 1.46 \times 10^{-4}$ s^{-1} and an initiator efficiency e of 0.6,[9] was only 3.8, we expect in any case zero-order decay of azobenzene, in agreement with experimental results.

It can be therefore concluded that only in the presence of a considerable amount of AIBN the reaction follows a radical pathway, while in the absence of initiator the participation of stannyl radicals must be ruled out. As a consequence we have also to discard a mechanism similar to the one suggested by Tanner et al. for the uninitiated Bu_3SnH reduction of ketones involving initial electron transfer to give a $Bu_3SnH^{+\bullet}$ cation which, by deprotonation, affords a stannyl radical behaving as the carrier of a radical chain reaction.[3]

As a possible reaction path we may consider either an heterolytic mechanism involving hydride transfer as shown in Scheme IV or an electron-transfer mechanism (eq 10), implying initial formation of the radical anion of the azoarene and the radical cation of tin hydride which then collapse to afford the hydrazo compound.



(10)

In both cases the reaction should be affected by the electronic properties of the substituents in the aryl rings of the azoarene; in fact, electron acceptors are expected to accelerate the reaction while the opposite effect should be observed with electron donors, in agreement with the experimental results for the 4-cyano- and 4-methoxyazobenzenes. In this respect it is worthwhile noting that aliphatic azo compounds are not reduced by tin hydride.[10]

Inconsistent with the hydride transfer mechanism is the fact that azoarenes are not reduced by very effective hydride transfer agents such as $LiAlH_4$ and $NaBH_4$, unless Lewis acids are also present.[5] On the other hand also a simple outer sphere electron-transfer process does not seem very likely on the basis of the following considerations. A reliable estimate of the energetics of the SET process is not possible since not all the required parameters are available. Actually, the one-electron reduction potential, $E°_{1/2}$(red), of azobenzene has been reported as −1.37 V vs SCE,[11] but the oxidation potential of tributyltin hydride is not known. The latter should presumably be greater than 1 V,[12] thus the free energy change involved in the electron-transfer process is expected to be >50 kcal/mol, a value too large with respect to the experimental activation energy (17.6 kcal/mol).

A possible explanation is that the reaction takes place via initial and reversible formation of a coordination complex between the tin compound and the azoarene, which then evolves to the products either by an inner sphere electron transfer or by an hydride transfer (Scheme V). Partial support for this hypothesis is provided by the value of log A (7.5), unusually small for a bimolecular reaction and indicative of a mechanism involving several steps. It should be emphasized that the equilibrium of Scheme V should be largely shifted to the left since no shifts in the absorption maxima nor appearance of new bands were observed in the visible spectra of **1a** in the presence of tin hydride.

EPR Measurements. In the presence of the radical initiator AIBN the products recovered in the reaction of iodo-substituted azoarenes and the marked increase of the rate constant are consistent with the involvement of stannyl radicals which would carry on the reduction according to the reaction sequence shown in Scheme II.

To check the feasibility of reaction 5, i.e., hydrogen abstraction from tin hydride by hydrazyl radicals, we reacted Bu_3SnH with DPPH, which is perhaps the least reactive hydrazyl known. The finding that DPPH is easily reduced indicates that indeed reaction 5 is possible.

As far as reaction 4 is concerned, a few examples have been reported in the literature of the addition of free radicals to the azo group. The available examples include addition of carbon-centered radicals to alkyl azodiformates[13,14] and of phenyl radicals to alkylaryl azo compounds.[15] With azoarenes only products of ring substitution are formed,[16] the intramolecular cyclization of 2′-(phenylazo)-2-biphenylyl radical to afford 1,2-dicarba-

(9) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1962**, *40*, 1851.

(10) Beckwith, A. L. J.; Wang, S.; Warkentin, J. *J. Am. Chem. Soc.* **1987**, *109*, 5289.

(11) Rao, P. S.; Hayon, E. *Anal. Chem.* **1976**, *48*, 564.

(12) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.

(13) Baigrie, B. D.; Cadogan, J. I. G.; Sharp, J. T. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1065. Lui, H.; Warkentin, J. *Can. J. Chem.* **1973**, *51*, 1148 and references cited therein.

(14) Leardini, R.; Nanni, D.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Chem. Commun.* **1989**, 757.

(15) Strausz, O. P.; Berkley, R. E.; Gunning, H. E. *Can. J. Chem.* **1969**, *47*, 3470. Kharasch, M. S.; Zimmermann, M.; Zimmt, W.; Nudenberg, W. *J. Org. Chem.* **1953**, *18*, 1045. Olaj, O. F.; Breitenbach, J. W.; Hofreiter, I. *Recl. Chem. Progr.* **1969**, *30*, 87.

(16) Miller, J.; Paul, D. B.; Wong, L. Y.; Kelso, A. G. *J. Chem. Soc. B* **1970**, 62.

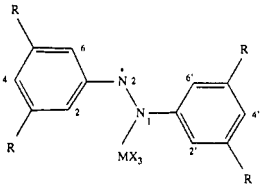
Table II. EPR Spectral Parameters (hfs Constants in Gauss = 10^{-4} T) for the Radical Adducts of Azoarenes 14 and 15 and of Benzo[*b*]cinnoline (16)

radical	MX_3	$a(N_1)$	$a(N_2)$	$a(H_{2,6})$	$a(H_{3,5})$	$a(H_4)$	$a(H_{2',4',6'})$	$a(H_{3',5'})$	g
14a	$SiPh_3$	4.00	10.94	3.52	1.24	4.16	0.64	<0.3	2.0038
14b	$GePh_3$	5.40	10.52	3.40	1.46	3.40	0.87	0.47	2.0037
14c	$SnBu_3$	spectrum unresolved; overall splitting ca. 42 G							2.0035
15a	$SiPh_3$	4.00	10.90	3.46		4.00	0.60		2.0037
15b	$GePh_3$	5.45	10.57	3.37		3.37	0.98		2.0035
16a	$SiPh_3$	4.05	8.37	3.52, H_2	1.28	4.64	1.28, $H_{2',4'}$	<0.3	2.0034
16b	$GePh_3$	spectrum unresolved; overall splitting ca. 40.2 G							2.0033
16c	$SnBu_3$	spectrum unresolved; overall splitting ca. 40.8 G							2.0030

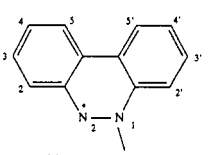
zol-9-yl-1,2-diphenylhydrazine being the only example of addition to the azo group.[8]

Examples of the direct characterization by EPR of spin adducts obtained by reacting free radicals with azo compounds are even fewer. Those available are the hydrazyls derived from azodicarboxylates,[17] chlorodiazirines,[18] and 4-phenyl-3*H*-1,2,4-triazole-2,5-dione.[19] In order to check whether stannyl and more generally group IVB organometallic radicals may give addition to simple azoarenes, they were reacted within the EPR cavity with azobenzene, 3,5,3′,5′-tetramethoxyazobenzene, and benzo[*c*]cinnoline. The methoxy-substituted azobenzene was chosen to simplify the EPR spectra by eliminating the couplings due to the meta protons of the two phenyl rings.

The organometallic radicals were generated in situ either by hydrogen abstraction from Ph_3SiH and Ph_3GeH by photolytically produced *tert*-butoxy radicals or by photolytic cleavage of the metal–metal bond of hexabutyldistannane, $Bu_3SnSnBu_3$. In the presence of azo compounds these radicals were trapped, giving rise to EPR spectra characteristic of the substituted hydrazyls **14–16** showing



14; R = H
15; R = OMe



16

large differences in the two nitrogen hyperfine splitting constants (see Table II), similar to that previously found for analogous organometallic hydrazyls.[17,19] It is worth pointing out that the tin radical adducts **14–16** could only be observed when photoreacting the pertinent azo compound with Bu_6Sn_2. When the tin radicals were generated by photolysis of Bu_3SnH, no EPR signals could be detected. This suggests that the hydrazyls are continuously subtracted from the system as the result of hydrogen abstraction from the tin hydride.

The combined effect of slow molecular motion and of anisotropy of the nitrogen hyperfine tensors resulted in a strong line-width dependence on the nitrogen spin quantum numbers, leading to much broader lines in the two wings of the spectra. This line-width broadening combined with the complexity of the spectral pattern made it hard to interpret the EPR spectra especially with the adducts of the more bulky radicals (germyl or stannyl). Thus, in some cases, only the *g* factor and the overall splitting of the spectra could be determined, which are also characteristic of hydrazyl adducts.

It is concluded that, at variance with carbon-centered radicals, group IVB radicals, including stannyls, may attack the nitrogen–nitrogen double bond of azoarenes to give substituted hydrazyls. This is therefore compatible with the proposed mechanism for the AIBN-initiated reduction of azoarenes by tributyltin hydride.

Experimental Section

General Procedures. Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^1H NMR spectra were recorded in deuteriochloroform on a Varian Gemini 200 (200 MHz) instrument, using tetramethylsilane as an internal standard. Mass spectra and high resolution mass spectra (HRMS) were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. Column chromatography was performed on silica gel (ICN Silica 63-200 60A), using a light petroleum ether (40–70 °C)/diethyl ether gradient as eluant.

Starting Materials. Tributyltin hydride (Aldrich), AIBN (Janssen), and diphenyldiazene (**1a**) were commercially available; AIBN was purified by being dissolved in chloroform and reprecipitated with methanol. Products **1b**,[20] **1c**,[21] **1d**,[22] **1e**,[20] **1f**,[23] **1g**,[23] **1h**,[21] **1i**,[24] **1j**,[24] **1k**,[25] **1l**,[26] **1n**,[23] **1o**,[23] **1p**,[23] **1q**,[27] **1r**,[28] **1s**,[29] **1t**,[30] **1v**,[31] **1w**,[23] **1x**,[32] 4-(phenylazo)phenol,[33] 3-(phenylazo)phenol,[34] 2-amino-2′-iodobiphenyl,[35] and 4-(nitrosomethyl)benzene[36] were prepared according to the literature.

Bis(3,5-dimethoxyphenyl)diazene (1m). 3,5-Dimethoxybenzenamine (1.53 g, 10 mmol) and PbO_2 (11.95 g, 10 mmol) in benzene (100 mL) were refluxed under mechanical stirring for 4 days with azeotropical removal of water. The hot mixture was filtered and the solid washed with hot benzene. The solvent was evaporated under vacuum and the residue chromatographed on silica gel to give **1m** (0.53 g, 35%): mp = 146–147 °C (from ethanol); 200-MHz ^1H NMR 3.89 (12 H, s, OCH_3), 6.61 (2 H, t, Ar *H*), 7.13 (4 H, d, Ar *H*); MS *m/e* (rel intensity) 302 (M^+, 32), 274 (9), 137 (100), 122 (64); HRMS calcd for $C_{16}H_{18}N_2O_4$ 302.12666, found 302.12642. Anal. Calcd for $C_{16}H_{18}N_2O_4$: C, 63.57; H, 6.00; N, 9.27. Found: C, 63.50; H, 6.02; N, 9.29.

1-[2-[(4-Hydroxy-1-naphthalenyl)azo]phenyl]ethanone. 1-(2-Aminophenyl)ethanone hydrochloride (1.71 g, 10 mmol) was diazotized, following the standard procedure, between 0 and 5 °C and added at room temperature to a solution of 1-hydroxynaphthalene (1.44 g, 10 mmol) and sodium hydroxide (1.20 g, 30 mmol) in water (50 mL). The title product precipitated and it was filtered, washed with water, and dried: yield = 2.49 g (86%); mp = 235–236 °C (from benzene); 200-MHz ^1H NMR 2.71 (3 H, s, CH_3), 6.75 (1 H, d, Ar *H*), 6.98–8.23 (9 H, m, Ar *H* + O*H*), 8.43 (1 H, d, Ar *H*); MS *m/e* (rel intensity) 290 (M^+, 100), 275 (5), 247 (12), 219 (7), 143 (8), 120 (24); HRMS calcd for $C_{18}H_{14}N_2O_2$

(17) Roberts, B. P.; Winters, J. N. *Tetrahedron Lett.* **1979**, *20*, 3575.
(18) Grugel, C.; Neumann, W. P. *Liebigs Ann. Chem.* **1979**, 870.
(19) Alberti, A.; Pedulli, G. F. *J. Org. Chem.* **1983**, *48*, 2544.
(20) Ritter, J. J.; Ritter, F. O. *J. Am. Chem. Soc.* **1930**, *52*, 2815.
(21) Jaffé, H. H.; Gardner, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 319.
(22) Jacobson, P.; Loeb, A. *Chem. Ber.* **1903**, *36*, 4082.
(23) Roling, P. V. *J. Org. Chem.* **1975**, *40*, 2421.
(24) Jacobson, P.; Steinbrenk, A. *Liebigs Ann. Chem.* **1898**, *303*, 384.
(25) McPherson, W. *Chem. Ber.* **1895**, *28*, 2414.
(26) Pentimalli, L. *Gazz. Chim. Ital.* **1960**, *90*, 1203.
(27) Grammaticakis, P. *Compt. Rend.* **1957**, *245*, 1145.
(28) Lock, G. *Chem. Ber.* **1930**, *63*, 855.
(29) Freundler, M. P. *Bull. Soc. Chim. Fr.* **1903**, *29*, 742.
(30) Lee, J. H.; Matsumoto, A.; Yoshida, M.; Simamura, O. *Chem. Lett.* **1974**, *9*, 951.
(31) Ruggli, P.; Hegedüs, B. *Helv. Chim. Acta* **1941**, *24*, 703.
(32) Goldschmidt, H.; Pollak, A. *Chem. Ber.* **1892**, *25*, 1324.
(33) Oddo, G.; Puxeddu, E. *Chem. Ber.* **1905**, *38*, 2752.
(34) Martynoff, M. *Compt. Rend.* **1946**, 747.
(35) Cade, J. A.; Pilbeam, A. *J. Chem. Soc.* **1964**, 114.
(36) Lutz, R. E.; Lytton, M. R. *J. Org. Chem.* **1938**, *2*, 68.

290.10553, found 290.10551. Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.39; H, 4.87; N, 9.67.

1-[2-[(4-Methoxy-1-naphthalenyl)azo]phenyl]ethanone (1u). To a solution of sodium ethoxide (0.68 g, 10 mmol) in absolute ethanol (100 mL) were added 1-[2-[(4-hydroxy-1-naphthalenyl)azo]phenyl]ethanone (2.90 g, 10 mmol) and, subsequently, iodomethane (1.42 g, 10 mmol), and the mixture was kept at 40 °C for 24 h. The solvent was evaporated and the residue chromatographed; elution with dichloromethane afforded **1u** (2.13 g, 70%): mp = 122–124 °C (from ethanol); 200-MHz ^{1}H NMR 2.58 (3 H, s, $COCH_3$), 4.10 (3 H, s, OCH_3), 6.91 (1 H, d, Ar *H*), 7.44–7.95 (7 H, m, Ar *H*), 8.32 (1 H, d, Ar *H*), 8.89 (1 H, d, Ar *H*); MS *m/e* (rel intensity) 304 (M^+, 54), 289 (15), 185 (7), 157 (100), 142 (10), 43 (9); HRMS calcd for $C_{19}H_{16}N_2O_2$ 304.12118, found 304.12102. Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 75.05; H, 5.28; N, 9.18.

[4-(Triphenylmethoxy)phenyl]phenyldiazene (1y). (4-Hydroxyphenyl)phenyldiazene sodium salt (2.20 g, 10 mmol), prepared from (4-hydroxyphenyl)phenyldiazene and sodium ethoxide in absolute ethanol, was refluxed for 3 h in benzene (30 mL) with chlorotriphenylmethane (2.78 g, 10 mmol). The solvent was evaporated and the residue chromatographed very quickly on silica gel, in order to minimize hydrolysis of the ether moiety, to give **1y** (2.86 g, 65%): mp = 146–148 °C (from benzene/ligroin 50:50 v/v); 200-MHz ^{1}H NMR 6.83 (2 H, d, Ar *H*), 7.17–7.50 (18 H, m, Ar *H*), 7.62 (2 H, d, Ar *H*), 7.76–7.85 (2 H, m, Ar *H*); MS *m/e* (rel intensity) 243 (M^+ – 197, 100), 165 (32), 77 (10). Anal. Calcd for $C_{31}H_{24}N_2O$: C, 84.52; H, 5.49; N, 6.36. Found: C, 84.47; H, 5.47; N, 6.34.

[3-(Triphenylmethoxy)phenyl]phenyldiazene (1z). Following the procedure described for **1y**, (3-hydroxyphenyl)-phenyldiazene sodium salt (2.20 g, 10 mmol) and chlorotriphenylmethane (2.78 g, 10 mmol) afforded **1z** (3.17 g, 72%) as an oil which could not be distilled: 200-MHz ^{1}H NMR 6.71–6.78 (1 H, m, Ar *H*), 7.03–7.54 (21 H, m, Ar *H*), 7.77–7.85 (2 H, m, Ar *H*); MS *m/e* (rel intensity) 243 (M^+ – 197, 100), 165 (21), 77 (6). Anal. Calcd for $C_{31}H_{24}N_2O$: C, 84.52; H, 5.49; N, 6.36. Found: C, 84.45; H, 5.51; N, 6.34.

[2-[2′-Iodo-(1,1′-biphenyl)]](4-methylphenyl)diazene (11). A solution of 2′-iodo-(1,1′-biphenyl)-2-amine (2.95 g, 10 mmol) and 4-(nitrosomethyl)benzene (1.21 g, 10 mmol) in glacial acetic acid (25 mL) was refluxed for 1 h. After cooling, the mixture was poured into water, neutralized with sodium carbonate, and extracted with diethyl ether. The organic phase was dried (sodium sulfate), the solvent was evaporated, and the residue was chromatographed on silica gel to give **11** (1.79 g, 45%): mp = 123–124 °C (from ethanol); 200-MHz ^{1}H NMR 2.30 (3 H, s, CH_3), 6.94–7.93 (12 H, m, Ar *H*); MS *m/e* (rel intensity) 271 (M^+ – 127, 100), 152 (30), 91 (22), 65 (8). Anal. Calcd for $C_{19}H_{15}IN_2$: C, 57.30; H, 3.80; I, 31.87; N, 7.03. Found: C, 57.35; H, 3.79; I, 31.82; N, 7.04.

General Procedure for the Reactions of Diazenes 1a–z and 11 with Tributyltin Hydride. A solution of azoarene (1 mmol) and tributyltin hydride (0.90 g, 3 mmol) in benzene (10 mL) was refluxed to complete disappearance of starting material (1–5 h). Concentration and cooling of the reaction mixture afforded solid hydrazines **2a–o** and **13** or cyclized products **7a–c** and **8**; the solid was collected and the filtrate chromatographed on silica gel. When the reaction yielded both hydrazo compounds **2p–s** and heterocycles **3**, **4**, **5**, and **6**, the solvent was completely evaporated and the residue chromatographed. According to this general procedure the following reactions were performed.

Reaction of 1a with Bu_3SnH. **1a** (0.18 g) gave, after a 4-h reflux, 1,2-diphenylhydrazine (**2a**) (0.17 g, 92%): mp = 126–127 °C (from ethanol), lit.[37] mp = 126–127 °C.

Reaction of 1b with Bu_3SnH. **1b** (0.20 g) gave, after a 5-h reflux, 1-(4-methylphenyl)-2-phenylhydrazine (**2b**) (0.18 g, 92%): mp = 86–87 °C (from ethanol), lit.[20] mp = 86–87 °C.

Reaction of 1c with Bu_3SnH. **1c** (0.21 g) yielded, after a 5-h reflux, 1-(4-methoxyphenyl)-2-phenylhydrazine (**2c**) (0.19 g, 89%): mp = 71–72 °C (from ethanol), lit.[38] mp = 72 °C.

Reaction of 1d with Bu_3SnH. **1d** (0.22 g) afforded, after a 3-h reflux, 1-(4-chlorophenyl)-2-phenylhydrazine (**2d**) (0.19 g, 87%): mp = 89–90 °C (from ethanol), lit.[39] mp = 90–91 °C.

Reaction of 1e with Bu_3SnH. **1e** (0.26 g) yielded, after a 3-h reflux, 1-(4-bromophenyl)-2-phenylhydrazine (**2e**) (0.22 g, 84%): mp = 114–115 °C (from ethanol), lit.[20] mp = 115 °C.

Reaction of 1f with Bu_3SnH. **1f** (0.31 g) afforded, after a 3-h reflux, 1-(4-iodophenyl)-2-phenylhydrazine (**2f**) (0.27 g, 87%): mp = 105–106 °C (from ethanol), lit.[40] mp = 105–106 °C.

Reaction of 1g with Bu_3SnH. **1g** (0.21 g) gave, after a 2-h reflux, 4-(2-phenylhydrazino)benzonitrile (**2g**) (0.19 g, 91%): mp = 167–168 °C (from ethanol); 200-MHz ^{1}H NMR 5.75 (1 H, s, –N*H*–), 6.00 (1 H, s, –N*H*–), 6.75–6.96 (5 H, m, Ar *H*), 7.19–7.31 (2 H, m, Ar *H*), 7.48 (2 H, d, Ar *H*); MS *m/e* (rel intensity) 209 (M^+, 32), 208 (4), 182 (6), 102 (25), 92 (100), 77 (32); HRMS calcd for $C_{13}H_{11}N_3$ 209.09530, found 209.09521. Anal. Calcd for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.58; H, 5.31; N, 20.11.

Reaction of 1h with Bu_3SnH. **1h** (0.22 g) afforded, after a 2-h reflux, 1-[4-(2-phenylhydrazino)phenyl]ethanone (**2h**) (0.20 g, 89%): mp = 164–165 °C (from ethanol); 200-MHz ^{1}H NMR 2.52 (3 H, s, CH_3), 5.74 (1 H, s, –N*H*–), 6.00 (1 H, s, –N*H*–), 6.77–7.30 (7 H, m, Ar *H*), 7.87 (2 H, d, Ar *H*); MS *m/e* (rel intensity) 226 (M^+, 100), 224 (10), 211 (16), 183 (30), 119 (18), 106 (37), 92 (63), 77 (58); HRMS calcd for $C_{14}H_{14}N_2O$ 226.11061, found 226.10998. Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.24; H, 6.26; N, 12.40.

Reaction of 1i with Bu_3SnH. **1i** (0.24 g) yielded, after a 2-h reflux, 4-(2-phenylhydrazino)benzoic acid methyl ester (**2i**) (0.22 g, 91%): mp = 115–116 °C (from ethanol), lit.[24] mp = 114–115 °C.

Reaction of 1j with Bu_3SnH. **1j** (0.23 g) afforded, after a 3-h reflux, 4-(2-phenylhydrazino)benzoic acid (**2j**) (0.19 g, 83%): mp = 192–193 °C (from ethanol), lit.[24] mp = 192–193 °C.

Reaction of 1k with Bu_3SnH. **1k** (0.30 g) gave, after a 3-h reflux, 4-(2-phenylhydrazino)phenol benzoate (**2k**) (0.26 g, 86%): mp = 172–173 °C (from ethanol), lit.[41] mp = 173 °C.

Reaction of 1l with Bu_3SnH. **1l** (0.18 g) yielded, after a 2-h reflux, 1-phenyl-2-(3-pyridyl)hydrazine (**2l**) (0.15 g, 81%): mp = 132–134 °C (from ethanol); 200-MHz ^{1}H NMR 5.75 (1 H, s, –N*H*–), 5.80 (1 H, s, –N*H*–), 6.78–7.32 (7 H, m, Ar *H*), 8.04–8.30 (2 H, m, Ar *H*); MS *m/e* (rel intensity) 185 (M^+, 100), 184 (18), 183 (5), 158 (12), 157 (14), 105 (34), 92 (64), 77 (32); HRMS calcd for $C_{11}H_{11}N_3$ 185.09530, found 185.09515. Anal. Calcd for $C_{11}H_{11}N_3$: C, 71.32; H, 5.99; N, 22.69. Found: C, 71.28; H, 6.00; N, 22.72.

Reaction of 1m with Bu_3SnH. **1m** (0.30 g) afforded, after a 4-h reflux, 1,2-bis(3,5-dimethoxyphenyl)hydrazine (**2m**) (0.27 g, 89%): mp = 109–110 °C (from ethanol): 200-MHz ^{1}H NMR 3.74 (12 H, s, CH_3), 5.57 (2 H, s, –N*H*–), 5.96–6.08 (6 H, m, Ar *H*); MS *m/e* (rel intensity) 304 (M^+, 100), 302 (21), 289 (10), 273 (15), 258 (8), 153 (23), 152 (13), 137 (46); HRMS calcd for $C_{16}H_{20}N_2O_4$ 304.14231, found 304.14205. Anal. Calcd for $C_{16}H_{20}N_2O_4$: C, 63.14; H, 6.62; N, 9.20. Found: C, 63.09; H, 6.64; N, 9.22.

Reaction of 1n with Bu_3SnH. **1n** (0.31 g) gave, after a 3-h reflux, 1-(2-iodophenyl)-2-phenylhydrazine (**2n**) (0.23 g, 74%): mp = 91–93 °C (from ethanol); 200-MHz ^{1}H NMR 5.73 (1 H, s, –N*H*–), 6.02 (1 H, s, –N*H*–), 6.54–7.33 (8 H, m, Ar *H*), 7.71 (1 H, d, Ar *H*); MS *m/e* (rel intensity) 310 (M^+, 100), 217 (28), 203 (9), 183 (25), 182 (48), 92 (30), 91 (55), 77 (48); HRMS calcd for $C_{12}H_{11}IN_2$ 309.99670, found 309.99597. Anal. Calcd for $C_{12}H_{11}IN_2$: C, 46.47; H, 3.58; I, 40.92; N, 9.03. Found: C, 46.42; H, 3.59; I, 40.94; N, 9.05.

Reaction of 1o with Bu_3SnH. **1o** (0.31 g) afforded, after a 3-h reflux, 1-(3-iodophenyl)-2-phenylhydrazine (**2o**) (0.27 g, 87%): mp = 93–94 °C (from ethanol); 200-MHz ^{1}H NMR 5.53 (1 H, s, –N*H*–), 5.56 (1 H, s, –N*H*–), 6.74–7.00 (5 H, m, Ar *H*), 7.11–7.30 (4 H, m, Ar *H*); MS *m/e* (rel intensity) 310 (M^+, 17), 308 (5), 218 (2), 203 (4), 184 (100), 183 (26), 92 (85), 77 (77); HRMS calcd for $C_{12}H_{11}IN_2$ 309.99670, found 309.99635. Anal. Calcd for $C_{12}H_{11}IN_2$: C, 46.47; H, 3.58; I, 40.92; N, 9.03. Found: C, 46.41; H, 3.57; I, 40.97; N, 9.05.

Reaction of 1p with Bu_3SnH. **1p** (0.21 g) gave, after a 1-h reflux, 2-(2-phenylhydrazino)benzonitrile (**2p**) (0.14 g, 67%) [mp = 103–104 °C (from ethanol); 200-MHz ^{1}H NMR 5.76 (1 H, s,

(37) Brand, K.; Steiner, J. *Chem. Ber.* **1922**, *55*, 875.
(38) Banthorpe, D. V.; Cooper, A. *J. Chem. Soc. B* **1968**, 605.
(39) Heumann, K.; Mentha, E. *Chem. Ber.* **1886**, *19*, 1686.
(40) Noelting, E.; Werner, P. *Chem. Ber.* **1890**, *23*, 3252.
(41) Goldschmidt, H.; Brubacher, R. *Chem. Ber.* **1891**, *24*, 2300.

-NH-), 6.41 (1 H, s, -NH-), 6.78–7.52 (9 H, m, Ar H); MS m/e (rel intensity) 209 (M^+, 96), 208 (23), 182 (9), 102 (18), 92 (100), 77 (27); HRMS calcd for $C_{13}H_{11}N_3$ 209.09530, found 209.09495. Anal. Calcd for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.57; H, 5.32; N, 20.11.] and 3-amino-2-phenyl-2H-indazole (**3**) (0.05 g, 24%) [mp = 143–144 °C (from light petroleum ether/benzene 50:50 v/v), lit.[42] mp = 143–144 °C].

Reaction of 1q with Bu_3SnH. **1q** (0.24 g) afforded, after a 1-h reflux, 2-(2-phenylhydrazino)benzoic acid methyl ester (**2q**) (0.06 g, 25%) [mp = 135–136 °C (from benzene/ligroin 50:50 v/v), lit.[43] mp = 136–136.5 °C] and 2-phenyl-1,2-dihydro-3H-indazol-3-one (**4**) (0.15 g, 71%) [mp = 215–216 °C (from ethanol), lit.[44] mp = 216 °C].

Reaction of 1r with Bu_3SnH. **1r** (0.30 g) gave, after a 1-h reflux, 2,2′-(1,2-hydrazino)bis(benzoic acid) dimethyl ester (**2r**) (0.19 g, 63%) [mp = 167–168 °C (from benzene/ligroin 50:50 v/v); 200-MHz ^1H NMR 3.92 (6 H, s, CH_3), 6.70–7.40 (6 H, m, Ar H), 7.92–8.00 (2 H, m, Ar H), 9.10 (2 H, s, -NH-); MS m/e (rel intensity) 300 (M^+, 33), 267 (2), 236 (100), 208 (12), 118 (11), 92 (4), 77 (6); HRMS calcd for $C_{16}H_{16}N_2O_4$ 300.11101, found 300.11087. Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.91; H, 5.39; N, 9.36.] and 6H,12H-indazolo-[2,1-a]indazole-6,12-dione (**5**) (0.07 g, 30%) [mp = 300–301 °C (from benzene), lit.[44] mp = 302 °C].

Reaction of 1s with Bu_3SnH. **1s** (0.21 g) afforded, after a 1-h reflux, 2-(2-phenylhydrazino)benzenemethanol (**2s**) (0.07 g, 33%) [mp = 89–91 °C (from ethanol); 200-MHz ^1H NMR 4.76 (2 H, s, $-CH_2-$), 5.68 (1 H, bs, OH), 6.61–7.33 (11 H, m, Ar H + -NH-); MS m/e (rel intensity) 214 (M^+, 35), 212 (5), 196 (56), 195 (100), 183 (3), 167 (4), 123 (7), 93 (37), 91 (34), 77 (38); HRMS calcd for $C_{13}H_{14}N_2O$ 214.11061, found 214.11056. Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.79; H, 6.61; N, 13.10.] and 2-phenyl-2H-indazole (**6**) (0.11 g, 57%) [mp = 81–82 °C (from light petroleum ether), lit.[29] mp = 83–84 °C].

Reaction of 1t with Bu_3SnH. **1t** (0.29 g) yielded, after a 1-h reflux, 2,3-diphenyl-2H-indazole (**7a**) (0.23 g, 83%): mp = 109–110 °C (from benzene/ligroin 50:50 v/v), lit.[30] mp = 109.5–110 °C.

Reaction of 1u with Bu_3SnH. **1u** (0.30 g) gave, after a 1-h reflux, 2-(4-methoxy-1-naphthalenyl)-3-methyl-2H-indazole (**7b**) (0.25 g, 87%): mp = 191–192 °C (from benzene/ethanol 50:50 v/v); 200-MHz ^1H NMR 2.40 (3 H, s, CH_3), 4.06 (3 H, s, OCH_3), 6.84–7.80 (9 H, m, Ar H), 8.34 (1 H, d, Ar H); MS m/e (rel intensity) 288 (M^+, 100), 273 (89), 258 (5), 245 (11), 204 (8); HRMS calcd for $C_{19}H_{16}N_2O$ 288.12626, found 288.12604. Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.71. Found: C, 79.06; H, 5.61; N, 9.73.

Reaction of 1v with Bu_3SnH. **1v** (0.39 g) yielded, after a 1-h reflux, 1-phenyl-1-[2-(3-phenyl-2H-indazol-2-yl)phenyl]methanone (**7c**) (0.33 g, 88%): mp = 130–131 °C (from ligroin); 200-MHz ^1H NMR 6.97–7.66 (18 H, m, Ar H); MS m/e (rel intensity) 374 (M^+, 100), 373 (14), 345 (50), 297 (74), 269 (34), 105 (5), 77 (10); HRMS calcd for $C_{26}H_{18}N_2O$ 374.14191, found 374.14167. Anal. Calcd for $C_{26}H_{18}N_2O$: C, 83.40; H, 4.85; N, 7.48. Found: C, 83.30; H, 4.86; N, 7.51.

Reaction of 1w with Bu_3SnH. **1w** (0.23 g) afforded, after a 1-h reflux, 5-aminoindazolo[2,3-a]quinazoline (**8**) (0.19 g, 81%): mp = 223–224 °C (from aqueous ethanol), lit.[45] mp = 223–224 °C.

Reaction of 1x with Bu_3SnH. **1x** (1.05 g, 3 mmol) gave, after a 24-h reflux and column chromatography of the complete reaction mixture, unreacted **1x** (0.18 g, 17%), N-(4-chlorophenyl)benzamide (**10**) (0.30 g, 43%) [mp = 193–194 °C (from ethanol), lit.[46] mp = 194 °C], and N-(2-hydroxy-5-methyl)benzamide (**9**) (0.24 g, 35%) [mp = 185–186 °C (from ethanol), lit.[47] mp not reported].

Reaction of 1y with Bu_3SnH. **1y** (0.44 g) yielded, after a 24-h reflux, triphenylmethane (0.23 g, 94%) [mp = 91–92 °C (from ethanol), lit.[48] mp = 92 °C] and 4-(phenylazo)phenol (0.18 g, 91%) [mp = 150–151 °C (from ethanol), lit.[33] mp = 150 °C].

Reaction of 1z with Bu_3SnH. **1z** (0.44 g) gave, after a 24-h reflux, unreacted starting material (0.15 g, 35%) and 1-[(3-triphenylmethoxy)phenyl]-2-phenylhydrazine (0.24 g, 55%): mp = 151–153 °C (from benzene/ethanol 50:50 v/v); 200-MHz ^1H NMR 5.24 (1 H, s, -NH-), 5.26 (1 H, s, -NH-), 6.17–6.29 (3 H, m, Ar H), 6.57–6.85 (4 H, m, Ar H), 7.09–7.45 (17 H, m, Ar H); MS m/e (rel intensity) 244 (M^+ – 198, 62), 243 (49), 198 (18), 167 (24), 165 (100), 93 (8), 77 (13). Anal. Calcd for $C_{31}H_{26}N_2O$: C, 84.13; H, 5.92; N, 6.33. Found: C, 83.98; H, 5.93; N, 6.34.

Reaction of 11 with Bu_3SnH. **11** (0.40 g) afforded, after a 24-h reflux, N-(9H-carbazol-9-yl)-4-methylbenzenamine (**12**) (0.02 g, 7%) [mp = 175–177 °C (from benzene/ligroin 50:50 v/v), lit.[49] mp = 175–177 °C] and 1-[2-[2′-iodo-(1,1′-biphenyl)]]-2-(4-methylphenyl)hydrazine (**13**) (0.36 g, 90%) [mp = 112–113 °C (from aqueous ethanol); 200-MHz ^1H NMR 2.27 (3 H, s, CH_3), 5.26 (1 H, s, -NH-), 5.50 (1 H, s, -NH-), 6.75–7.52 (11 H, m, Ar H), 8.01 (1 H, d, Ar H); MS m/e (rel intensity) 400 (M^+, 92), 273 (30), 271 (100), 167 (93), 106 (90), 91 (37), 77 (21); HRMS calcd for $C_{19}H_{17}IN_2$ 400.04365, found 400.04323. Anal. Calcd for $C_{19}H_{17}IN_2$: C, 57.01; H, 4.28; I, 31.71; N, 7.00. Found: C, 56.95; H, 4.29; I, 31.74; N, 7.02.].

Reaction of 11 with Bu_3SnH in the Presence of 2% AIBN. Following the procedure previously described, but in the presence of AIBN (0.003 g, 0.02 mmol), **11** (0.40 g) gave, after a 24-h reflux, **12** (0.05 g, 18%) [mp = 176–177 °C, lit.[49] mp = 175–177 °C] and **13** (0.25 g, 63%) [mp = 112–113 °C (from aqueous ethanol)].

Reaction of 11 with Bu_3SnH in the Presence of 25% AIBN. Following the procedure previously described, but in the presence of AIBN (0.04 g, 0.25 mmol), **11** (0.40 g) gave, after a 6-h reflux, **12** (0.23 g, 85%) [mp = 175–177 °C, lit.[49] mp = 175–177 °C] and **13** (0.03 g, 7%) [mp = 111–113 °C (from aqueous ethanol)].

Reaction of 1n with Bu_3SnH in the Presence of 2% AIBN. Following the standard procedure described above, but in the presence of AIBN (0.01 g, 0.06 mmol), **1n** afforded, after a 24-h reflux, **1a** (0.07 g, 13%) [mp = 68–69 °C], [2-(1,1′-biphenyl)]-phenyldiazene (trace amounts) [mp = 38–39 °C (from ethanol), lit.[50] mp = 37–39 °C], **2n** (0.63 g, 68%) [mp = 92–93 °C], and **2a** (0.04 g, 7%) [mp = 126–127 °C, lit.[37] mp = 126–127 °C].

Reaction of 1n with Bu_3SnH in the Presence of 25% AIBN. Following the procedure previously described, but in the presence of AIBN (0.12 g, 0.75 mmol), **1n** gave, after a 24-h reflux, **1a** (0.10 g, 18%) [mp = 68–69 °C], [2-(1,1′-biphenyl)]phenyldiazene (0.05 g, 6%) [mp = 38–39 °C, lit.[50] mp = 37–39 °C], **2n** (0.38 g, 41%) [mp = 92–93 °C], and **2a** (0.12 g, 22%) [mp = 125–127 °C, lit.[37] mp = 126–127 °C].

EPR and Kinetic Measurements. EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with a Hewlett Packard 5350B frequency counter for the determination of the g factors which were corrected with respect to that of the perylene radical cation (2.00258). Photolysis was carried out with the light from a 500-W high pressure mercury lamp.

Kinetic measurements were done by following spectrophotometrically the decrease of the absorbance due to the azo compound at 448 nm. The concentrations of Bu_3SnH in benzene or *tert*-butylbenzene solutions were in the range 0.25–2 M and those of the azoarene in the range 0.025–1 M. Samples taken at regular time intervals from the solution kept at fixed temperature were diluted before measuring the absorbance.

Acknowledgment. Financial support from "Progetto Finalizzato del CNR: Chimica Fine II" and from Ministero della Pubblica Istruzione (MPI, Rome) is gratefully acknowledged.

Registry No. **1a**, 103-33-3; **1b**, 949-87-1; **1c**, 2396-60-3; **1d**, 4340-77-6; **1e**, 4418-84-2; **1f**, 6639-27-6; **1g**, 1837-93-0; **1h**, 4827-16-1; **1i**, 2918-88-9; **1j**, 1562-93-2; **1k**, 16513-94-3; **1l**, 2569-55-3; **1m**, 137720-85-5; **1n**, 51343-11-4; **1o**, 23377-17-5; **1p**, 38302-59-9; **1q**, 36038-91-2; **1r**, 17277-29-1; **1s**, 137720-83-3; **1t**, 54184-68-8; **1u**, 137720-95-7; **1v**, 70593-68-9; **1w**, 16288-72-5; **1x**, 137720-84-4; **1y**, 137720-96-8; **1z**, 137720-97-9; **2a**, 122-66-7; **2b**, 621-94-3; **2c**,

(42) Partridge, M. W.; Stevens, M. F. G. *J. Chem. Soc.* **1964**, 3663.
(43) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 313.
(44) Gibson, G. K. J.; Lindsey, A. S.; Paisley, H. M. *J. Chem. Soc. C* **1967**, 1792.
(45) Stevens, M. F. G. *J. Chem. Soc. C* **1967**, 1096.
(46) Emmerling, O. *Chem. Ber.* **1875**, *8*, 880.
(47) Courdet, G.; Guillaumet, G.; Loubinoux, B. *Synthesis* **1979**, *7*, 541.
(48) Norris, J. F.; Young, R. C. *J. Am. Chem. Soc.* **1924**, *46*, 2580.
(49) Benati, L.; Spagnolo, P.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1536.
(50) Risaliti, A.; Stener, A. *Ann. Chim.* **1967**, *57*, 3.

953-12-8; **2d**, 949-88-2; **2e**, 7466-30-0; **2f**, 137720-86-6; **2g**, 137720-87-7; **2h**, 6311-55-3; **2i**, 137720-88-8; **2j**, 7400-25-1; **2k**, 137720-89-9; **2l**, 17999-52-9; **2m**, 137720-90-2; **2n**, 137720-91-3; **2o**, 137720-92-4; **2p**, 137721-01-8; **2q**, 20217-91-8; **2r**, 137721-02-9; **2s**, 137721-03-0; **3**, 1019-13-2; **4**, 17049-65-9; **5**, 18428-89-2; **6**, 3682-71-1; **7a**, 54184-69-9; **7b**, 137720-93-5; **7c**, 137720-94-6; **8**, 16288-73-6; **9**, 93-63-0; **10**, 2866-82-2; **11**, 137721-00-7; **12**, 71903-22-5; **13**, 137721-04-1; **14a**, 137721-05-2; **14b**, 137721-06-3; **14c**, 137721-07-4; **15a**, 137721-08-5; **15b**, 137721-09-6; **16a**, 137721-10-9; **16b**, 137721-11-0; **16c**, 137721-12-1; Bu_3SnH, 688-73-3; Ph_3SiH, 789-25-3; Ph_3GeH, 2816-43-5; Bu_6Sn_2, 813-19-4; 4-(phenylazo)phenol, 1689-82-3; 3-(phenylazo)phenol, 2437-11-8; 2-amino-2′-iodobiphenyl, 54147-90-9; 4-(nitrosomethyl)benzene, 623-11-0; 3,5-dimethoxybenzenamine, 10272-07-8; 1-(2-aminophenyl)ethanone, 25384-14-9; 1-hydroxynaphthalene, 90-15-3; 1-[2-[(4-hydroxy-1-naphthalenyl)azo]phenyl]ethanone, 137720-98-0; (4-hydroxyphenyl)phenyldiazene, 51451-39-9; (3-hydroxyphenyl)phenyldiazene sodium salt, 137720-99-1; chlorotriphenylmethane, 76-83-5; triphenylmethane, 519-73-3; 1-[(3-triphenylmethoxy)phenyl]-2-phenylhydrazine, 137721-13-2.

Mechanism of Oxygen Atom Transfer from Oxaziridine to a Lithium Enolate. A Theoretical Study

Robert D. Bach* and José L. Andrés

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Franklin A. Davis

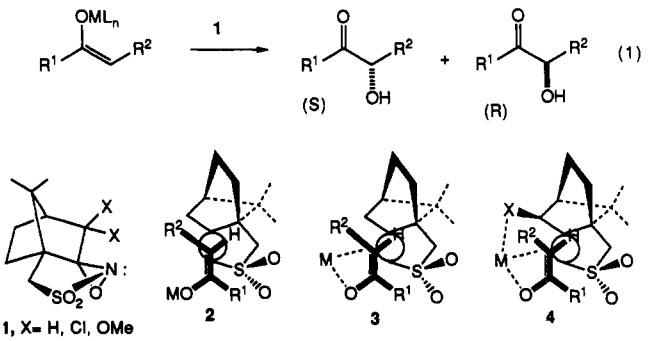
Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Received January 9, 1991

The asymmetric enolate oxidation protocol employing enantiopure *N*-sulfonyloxaziridines is highly successful in the synthesis of enantiomerically enriched α-hydroxy carbonyl compounds. Molecular orbital calculations at the HF/6-31+G*//HF/4-31+G level have been used on a model system to elucidate the structural and electronic features of the transition state for oxygen atom transfer. Oxidation of the lithium enolate of acetaldehyde proceeds by S_N2 attack of the β-carbon on the enolate along the O–N bond of the parent oxaziridine. In the transition state the lithium cation is coordinated to both the enolate and the oxaziridine oxygen atoms. Model studies suggest that the sulfonyl oxygen atom is also bound to the metal cation, influencing the stereoselectivity of the resulting α-hydroxy carbonyl compound.

Introduction

The asymmetric synthesis of α-hydroxy carbonyl compounds is a subject of considerable current interest because this structural unit is featured in many natural products.[1] Furthermore these compounds are useful chiral building blocks in the synthesis of biologically active materials.[2] An important strategy in the chiral synthesis of these materials is the asymmetric α-hydroxylation of an enolate anion using an enantiomerically pure (camphorylsulfonyl)oxaziridine, **1**, oxidizing reagent (eq 1).[1,3,4] Stereoselectivities



for oxygen transfer of better than 95% ee are often realized.[1,4–6] From the structure reactivity trends the results were generally interpreted in terms of an "open" transition state dominated by nonbonded steric interactions with minimal direct influence of the metal cation, i.e. **2**.[1,3,5] In this model the reasonable assumption was made that the metal oxygen moiety is the sterically most demanding group in the region of the enolate anion.

While this simple model has proven useful in rationalizing the molecular recognition, in many cases the stereoselectivities are frequently unpredictable. Recent studies have shown that the absolute stereochemistry of the products are dependent upon (i) the structure of the enolate, (ii) the oxidant, and (iii) the reaction conditions.[1,3] Undoubtedly this imprecision is related to a lack of knowledge of the transition-state structures (TS) as well as difficulty in relating the aggregated solution structure of the enolate to its reactivity.[3] Recent studies of the asymmetric oxidation of tetralone enolate derivatives using **1** (X = Cl or OMe) has suggested the possibility of transition-state stabilization via chelation of the metal enolate with the oxaziridine **3** or a substituent X, **4**; i.e. a "closed" transition state.[1,4,6]

In earlier theoretical studies on oxygen atom transfer from oxaziridine to an alkene,[7a] one of the major objectives was to identify any electronic effects pertaining to the approach of the reactants that would favor a planar versus a spiro transition state (Figure 1). It had been anticipated[7a] that the higher energy π-type lone pair on the oxaziridine oxygen could interact with the π* orbital of the alkene undergoing epoxidation in a spiro orientation resulting in a two-electron stabilization of the TS. At the

(1) Davis, F. A.; Sheppard, A. C.; Chen, B. C.; Haque, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 6679.
(2) Hannessian, S. *Total Synthesis of Natural Products: the Chiron Approach*, Pergamon Press; New York, 1983; Chapter 2.
(3) For a review on the chemistry of *N*-sulfonyloxaziridines which includes a section on enolate oxidations by these reagents, see: Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703.
(4) (a) Davis, F. A.; Weismiller, M. E. *J. Org. Chem.* **1990**, *55*, 3715. (b) Davis, F. A.; Chen, B.-C. *Tetrahedron Lett.* **1990**, *31*, 6823.
(5) Chen, B.-C.; Weismiller, M. C.; Davis, F. A.; Boschelli, D.; Empfield, J. R.; Smith, A. B. III *Tetrahedron* **1991**, *47*, 173.
(6) Davis, F. A.; Kumar, A.; Chen, B.-C. *J. Org. Chem.* **1991**, *56*, 1143.
(7) (a) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1410. (b) Bach, R. D.; Coddens, B. A.; McDouall, J. J. W.; Schlegel, H. B.; Davis, F. A. *J. Org. Chem.* **1990**, *55*, 3325.

0022-3263/92/1957-0613$03.00/0