(1), 158 (84), 96 (25), 81 (54), 69 (48), 67 (81), 41 (100). Anal. Calcd for $C_{12}H_{15}N_3Se$: C, 51.43; H, 5.40; N, 14.99. Found: C, 51.48; H, 5.52; N, 15.03.

1-(Azidomethyl)cyclopentene (14) and (azidomethylene)cyclopentane (15): IR (neat) 2100 cm^{-1}; ^{1}H NMR δ (14) 5.72–5.65 (m, 1 H), 3.9–3.78 (bs, 2 H), 2.5–2.3 (m, 4 H), 2.02–1.88 (m, 2 H); (15) 5.18–5.1 (m, 1 H), 2.5–2.3 (m, 8 H); ^{13}C NMR δ (14) 138.5, 129.4, 51.4, 33.4, 32.4, 23.5 (15) 138.5, 131.7, 32.9, 23.0; MS *m/e* (rel intensity) (14) 123 (M, 10), 95 (12), 94 (36), 81 (52), 68 (33), 67 (100), 55 (40), 41 (93); (15) 123 (M, 7), 91 (21), 94 (50), 81 (49), 68 (30), 67 (100), 55 (37), 41 (87). Anal. Calcd for $C_6H_9N_3$: C, 58.52; H, 7.37; N, 34.12. Found: C, 58.58; H, 7.46; N, 34.18.

1-(Azidomethyl)-2-[(phenylseleno)methyl]cyclopentane (19): oil; IR (neat) 2090 cm^{-1}; ^{1}H NMR δ 7.6–7.4 (m, 2 H), 7.3–7.1 (m, 3 H), 3.34 (dd, 1 H, *J* = 6.5 and 12.2 Hz), 3.18 (dd, 1 H, *J* = 7.7 and 12.2 Hz), 2.98 (dd, 1 H, *J* = 5.9 and 11.5 Hz), 2.76 (dd, 1 H, *J* = 9.0 and 11.5 Hz), 2.35–2.15 (m, 2 H), 2.0–1.3 (m, 6 H); ^{13}C NMR δ 132.5, 130.5, 128.9, 126.7, 52.0, 42.1, 42.0, 31.4, 29.0, 28.9, 22.5; MS *m/e* (rel intensity) 295 (1), 185 (34), 171 (13), 157 (45), 110 (38), 91 (37), 81 (100), 67 (27), 55 (22), 41 (57). Anal. Calcd for $C_{13}H_{15}N_3Se$: C, 53.43; H, 5.17; N, 14.38. Found: C, 53.51; H, 5.29; N, 14.45.

7-Azido-6-(phenylseleno)-1-heptene (20): oil, IR (neat) 2100 cm^{-1}; ^{1}H NMR δ 7.7–7.5 (m, 2 H), 7.3–7.1 (m, 3 H), 5.9–5.63 (m, 1 H), 5.1–4.9 (m, 2 H), 3.55 (dd, 1 H, *J* = 5.4 and 12.5 Hz), 3.38 (dd, 1 H, *J* = 7.5 and 12.5 Hz), 3.3–3.15 (m, 1 H), 2.3–1.5 (m, 6 H); ^{13}C NMR δ 138.0, 135.2, 133.2, 129.1, 127.9, 114.9, 55.9, 44.4, 33.2, 31.9, 26.7; MS *m/e* (rel intensity) 295 (5), 267 (4), 172 (10), 110 (77), 106 (31), 91 (42), 78 (81), 67 (64), 41 (100). Anal. Calcd for $C_{13}H_{17}N_3Se$: C, 53.06; H, 5.82; N, 14.28. Found: C, 52.97; H, 5.75; N, 14.25.

1,7-Diazido-2,6-bis(phenylseleno)heptane (21): oil; IR (neat) 2090 cm^{-1}; ^{1}H NMR δ 7.6–7.45 (m, 8 H), 7.35–7.15 (m, 12 H), 3.55 (dd, 2 H, *J* = 5.3 and 12.5 Hz), 3.54 (dd, 2 H, *J* = 5.4 and 12.5 Hz), 3.41 (dd, 2 H, *J* = 7.4 and 12.5 Hz), 3.38 (dd, 2 H, *J* = 7.5 and 12.5 Hz), 3.2–3.05 (m, 4 H), 1.9–1.4 (m, 12 H); ^{13}C NMR δ 135.3, 133.1, 129.1, 128.0, 55.8, 44.2, 44.0, 32.0, 31.9, 25.6, 25.5. Anal. Calcd for $C_{19}H_{22}N_6Se_2$: C, 46.35; H, 4.50; N, 17.07. Found: C, 46.41; H, 4.61; N, 17.11.

1-(Azidomethyl)-4-[2-(phenylseleno)propyl]cyclohexane (25): oil; IR (neat) 2090 cm^{-1}; ^{1}H NMR δ 7.7–7.6 (m, 2 H), 7.4–7.2 (m, 3 H), 5.7–5.65 (m, 1 H), 3.7–3.5 (m, 2 H), 2.4–1.2 (m, 12 H); ^{13}C NMR δ 138.3, 132.4, 128.4, 128.3, 127.7, 126.2, 57.0, 51.3, 44.0, 28.2, 27.7, 27.4, 26.5, 25.0; MS *m/e* (rel intensity) 177 (M^{+} − PhSeH, 7), 158 (35), 150 (56), 135 (25), 108 (100), 106 (52), 91 (30), 78 (44), 67 (28), 41 (36). Anal. Calcd for $C_{16}H_{21}N_3Se$: C, 57.48; H, 6.33; N, 12.57. Found: C, 57.55; H, 6.46; N, 12.60.

1-(Azidomethyl)-4-(1-methylethenyl)cyclohexene (26): oil; IR (neat) 2090 cm^{-1}; ^{1}H NMR δ 5.8–5.7 (m, 1 H), 4.8–4.68 (m, 2 H), 3.72–3.58 (m, 2 H), 2.4–1.74 (m, 10 H): ^{13}C NMR δ 149.1, 132.2, 126.2, 108.9, 57.4, 40.7, 30.4, 27.3, 27.1, 20.7; MS *m/e* (rel intensity) 149 (M^{+} − N_2, 14), 134 (37), 106 (33), 93 (44), 91 (60), 68 (100), 67 (87), 53 (46), 41 (63). Anal. Calcd for $C_{10}H_{15}N_3$: C, 67.76; H, 8.53; N, 23.71. Found: C, 67.71; H, 8.49; N, 23.69.

2-Azido-1-(phenylseleno)ethyl crotonate (34): oil; IR (neat) 2100 and 1730 cm^{-1}; ^{1}H NMR δ 7.6–7.5 (m, 2 H), 7.4–7.2 (m, 3 H), 7.06 (dq, 1 H, *J* = 6.8 and 15.5 Hz), 6.29 (dd, 1 H, *J* = 5.3 and 7.8 Hz), 5.88 (dq, 1 H, *J* = 1.7 and 15.5 Hz), 3.56–3.52 (m, 2 H), 1.91 (dd, 3 H, *J* = 1.7 and 6.8 Hz); ^{13}C NMR δ 164.4, 146.7, 136.2, 129.1, 128.8, 121.7, 72.3, 54.8, 18.0; MS *m/e* (rel intensity) 311 (1), 157 (7), 154 (8), 77 (9), 69 (100), 51 (6), 41 (15). Anal. Calcd for $C_{12}H_{13}N_3O_2Se$: C, 46.30; H, 4.21; N, 13.51. Found: C, 46.37; H, 4.30; N, 13.55.

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Registry No. **1**, 116316-13-3; **2**, 73501-69-6; **3**, 136061-58-0; **4**, 136061-59-1; **5**, 136061-60-4; **6**, 136061-61-5; **7**, 136061-62-6; **8**, 136061-63-7; **9** (isomer 1), 136061-64-8; **9** (isomer 2), 136061-70-6; *cis*-**10**, 136061-65-9; *trans*-**10**, 116316-04-2; **11**, 116316-12-2; **12**, 136061-66-0; **13**, 136061-67-1; **14**, 136061-68-2; **15**, 136061-69-3; **16**, 3070-53-9; *cis*-**19**, 136061-71-7; *trans*-**19**, 136061-79-5; **20**, 136061-72-8; **21** (isomer 1), 136088-50-1; **21** (isomer 2), 136061-80-8; **22**, 127-91-3; **25**, 136061-73-9; **26**, 136061-74-0; **27**, 110-87-2; **28**, 136061-75-1; **29**, 136061-76-2; **30**, 96-33-3; **31**, 136061-77-3; **32**, 16717-78-5; **33**, 3234-54-6; **34**, 136061-78-4; NaN_3, 26628-22-8; $(PhSe)_2$, 1666-13-3; styrene, 100-42-5; 1-octene, 111-66-0; allylbenzene, 300-57-2; 5-hexen-2-one, 109-49-9; methyl 3-butenoate, 3724-55-8; methyl 4-pentenoate, 818-57-5; methyl 5-hexenoate, 2396-80-7; methylenecyclopentane, 1528-30-9; (*E*)-4-octene, 14850-23-8; cyclohexene, 110-83-8.

Supplementary Material Available: Physical and spectral data of compounds **9**, **10**, **3**, **5**, **6**, **7** (3 pages). Ordering information is given on any current masthead page.

Addition of Semidione Radicals to Arenediazonium Ions: Synthesis of 1,1-Diacyl-2-arylhydrazines

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The α-dicarbonyl compounds **1** are selectively reduced to semidione radicals **2** by aqueous Ti^{3+}, via inner-sphere electron transfer (ET). When an equimolar amount of an arenediazonium salt (**3**) is present, **2** adds to the nitrogen–nitrogen triple bond of **3** to afford the intermediate azo radical cation C, which, depending on the nature of the para substituent of the *N*-phenyl ring, undergoes rearrangement to a 1,1-diacyl-2-arylhydrazine (**4**) or preferentially reduction to a hydrazone (**5**). A mechanism that accounts for both the rearrangement and the substituent effects that are observed is proposed.

We recently showed[1] that the α-dicarbonyl compounds **1a,b,d** are reduced by aqueous titanium trichloride to the intermediate semidone radicals **2**. These stereoselectively add to the carbonyl group of aldehydes to afford α,β-dihydroxy ketones (Scheme I).

It was postulated that the addition proceeds via a radical-chelated Ti(IV) species (**2**). Chelation would restrict the number of possible transition states and would thereby lead to stereoselective addition.

We now report that, under similar experimental conditions, radicals **2a–d** add to the nitrogen–nitrogen triple bond of arenediazonium ions **3** to give, via the intermediate

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(1) Clerici, A.; Porta, O. *J. Org. Chem.* **1989**, *54*, 3872.

(2) Biacetyl (**1c**) undergoes reductive dimerization on treatment with Ti^{3+}. Clerici, A.; Porta, O. Unpublished results.

0022-3263/91/1956-6813$02.50/0

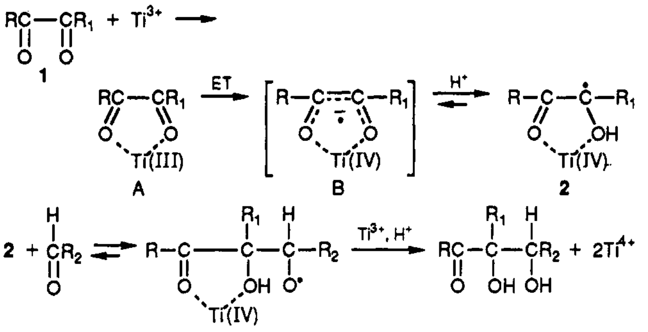
Table I. Yields[a] of Products Isolated from the Ti^{3+}-Mediated Reaction at 20 °C (Ar = *p*-XC_6H_4)

$$\underset{\mathbf{1a\text{-}d}}{RCO\text{—}COR_1} + N{\equiv}\underset{\mathbf{3}}{N^+}\text{—}Ar \rightarrow \underset{\mathbf{4}}{RCO\text{—}N(CO\text{—}R_1)NHAr} + \underset{\mathbf{5}}{RCO\text{—}C(R_1){=}NNHAr} + \underset{\mathbf{6}}{RCO\text{—}NHNHAr} + \underset{\mathbf{6'}}{R_1CO\text{—}NHNHAr}$$

				yield (%)					
entry	R	R_1	*p*-X	4	6	6′	5	recovered 1	ratio 1:Ti^{3+}
a	Ph	Ph	Cl	52	12		tr	30	1:2
				57	14		2	24[b]	1:3
b	Ph	Ph	H	65	10		tr	15	1:2
				70	12		6	5[b]	1:3
				30	40		7	12[b]	1:3[c]
c	Ph	Ph	CH_3	70	7		10	trace	1:2
				70	8		20		1:3
				38	40		18		1:3[c]
d	Ph	Ph	OCH_3	34	8		28	25	1:2
				48	tr		45		1:3
e	Ph	CH_3	Cl	25	18	17	15	21	1:2
				20	25	23	20	trace	1:3
f	Ph	CH_3	H	35	22	10	28	trace	1:3
					40	25	29		1:3[c]
g	Ph	CH_3	CH_3	23	22	10	42		1:3
h	Ph	CH_3	OCH_3		12	5	42	30	1:2
					20	7	63	trace	1:3
i	CH_3	CH_3	H		65		16	nd[d]	1:3
j	CH_3	CH_3	CH_3		67		20	nd[d]	1:3
k	CH_3	CH_3	OCH_3		58		30	nd[d]	1:3
l	Ph	H	Cl	75[e]					1:3
m	Ph	H	H	50[e]					1:3

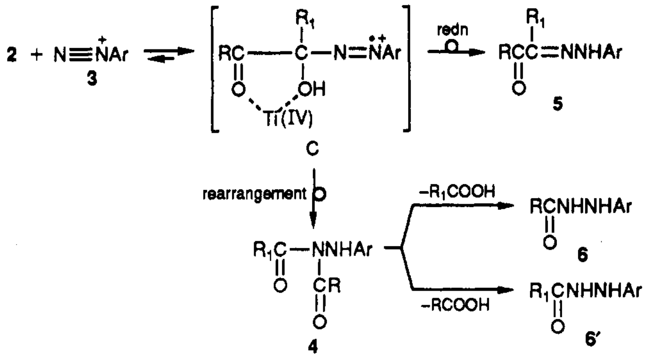
[a] Yields are based on the starting α-dicarbonyl compound 1. [b] Yields of benzoin. [c] Reaction performed at 50 °C. [d] nd = not determined, due to the low boiling point of 1c (88^{760} °C). [e] Yield of 1-(phenylglyoxyl)-2-arylhydrazine 7 (Scheme III).

Scheme I[a]



[a] 1a: R = R_1 = Ph; 1b: R = Ph, R_1 = CH_3; 1c: R = R_1 = CH_3;[2] 1d: R = Ph, R_1 = H.

Scheme II[a]



[a] Ar = *p*-XC_6H_4. X = H, Cl, CH_3, OCH_3.

azo radical cation C, 1,1-diacyl-2-arylhydrazines 4 and hydrazones 5 (Scheme II). Hydrolysis of 4, under the reaction conditions, affords the monoacylhydrazines 6 and 6′.

The two types of reactions outlined in Schemes I and II are mechanistically analogous. Because it is a nucleophile, 2 can attack an electron-deficient center to give a strongly electrophilic radical adduct. The rapidity of both the reduction of the intermediate alkoxyl radical (Scheme I) and the reduction or rearrangement of the azo radical cation C (Scheme II) makes the initial addition step practically irreversible in both cases, and thus the final products are formed in synthetically useful yields. That alkyl and β-hydroxyalkyl radicals ($R^\bullet$) add to diazonium ions was inferred from the results of kinetic studies.[3] Such additions were later shown[4] to be synthetically useful (eq 1). In contrast, α-hydroxyalkyl radicals (α-$R^\bullet$) failed to give any products of addition, because electron transfer from the radical to 3, rather than addition, occurs[3-5a] (eq 2).

$$R^\bullet + \mathbf{3} \rightarrow RN{=}\overset{\bullet+}{N}Ar \xrightarrow{\text{redn}} RN{=}NAr \qquad (1)$$

$$\alpha\text{-}R^\bullet + \mathbf{3} \xrightarrow{\text{ET}} \alpha\text{-}R^+ + {}^\bullet N{=}NAr \rightarrow N_2 + Ar^\bullet \qquad (2)$$

In the case described here, the addition of 2 to 3, rather than electron transfer, occurs, because the reducing properties of 2, due the presence of a "dative" α-OH group, are considerably diminished by the "capto" α-acyl substitution.[6]

Results and Discussion

Allowing a mixture of 1 (10 mmol) and an arenediazonium tetrafluoroborate (10 mmol) in glacial acetic acid (150 mL) to react for 40 minutes at 20 °C with 15% aqueous acidic titanium trichloride (20 or 30 mmol) led to the formation of 4, 5, 6, and 6′ (Scheme II) and the

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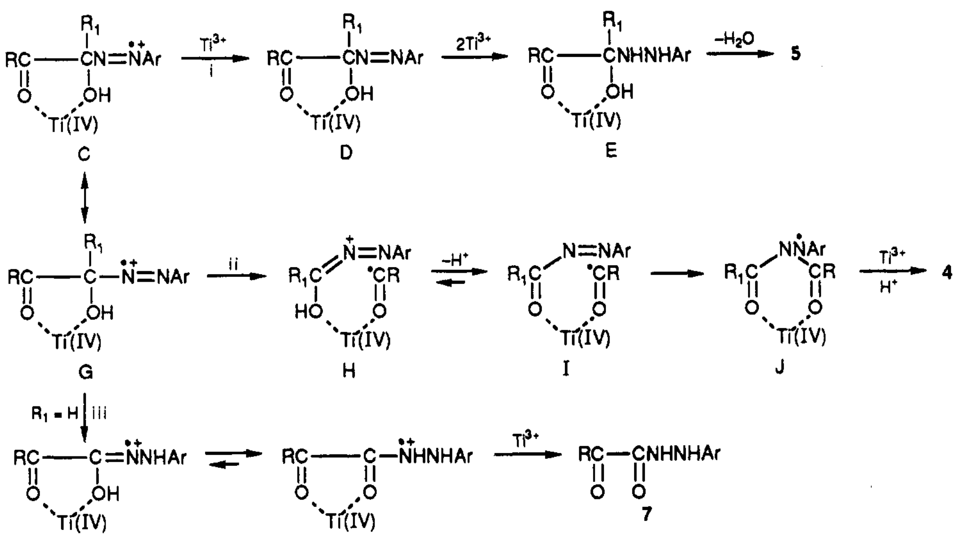
(3) (a) Heighway, C. J.; Packer, J. E.; Richardson, R. K. *Tetrahedron Lett.* **1974**, *38*, 4441. (b) Packer, J. E.; Richardson, R. K. *J. Chem. Soc., Perkin Trans. II* **1975**, 751.

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

(5) (a) Beckwith, A.; Norman, R. O. C. *J. Chem. Soc. B* **1969**, 404. (b) Galli, C. *Chem. Rev.* **1988**, *88*, 765.

(6) Rao, P. S.; Hayon, E. *J. Am. Chem. Soc.* **1974**, *96*, 1287.

Scheme III



concomitant discharge of the blue color due to Ti^{3+}. After workup, flash chromatography of the residue on silica gel afforded the products in the yields shown in Table I.

Selective Reduction of α-Dicarbonyl Compounds 1. It is well known[5] that Ti^{3+} rapidly reduces arenediazonium ions 3 to aryl radicals, with vigorous evolution of N_2. Under the reaction condition employed here, no (when X = CH_3, OCH_3) or very little (when X = H, Cl)[7] N_2 was evolved, even though the half-wave reduction potentials ($E_{1/2}$) indicate that 3 (when X = H, $E_{1/2} = -0.18$ V vs SCE at pH = 0)[8] is more easily reduced than benzil (**1a**) ($E_{1/2} = -0.27$ V vs SCE at pH = 1.3).[8] Because the half-wave potential ($E_{1/2}$ vs Hg pool)[9] becomes progressively more negative as one goes from benzil (**1a**) (−0.53 V) to benzoylacetone (**1b**) (−0.60 V) to biacetyl (**1c**) (−0.74 V), **3** should be even more easily reduced than **1b** and **1c**. On the other hand, the total yields of the products **4**, **5**, **6**, and **6′**, which retain both of the nitrogen atoms of the diazonium ion, are always very high.

Mechanistically, the selective and, in some cases, the quantitative[7] reduction of 1 in the presence of an equimolar amount of 3 can be explained in terms of the intermediacy of a five-membered chelate complex, A (Scheme I). When electron-rich compounds like 1 serve as ligands in chelate compounds that incorporate metal-ion electrophiles like Ti^{3+}, the reduction potential of such ligands becomes higher as a result of chelation[10] and, consequently, the barrier to inner-sphere electron transfer is lowered. Following such activation of the precursor complex A, selective electron transfer from Ti^{3+} to the ligand 1 would occur and thereby yield the Ti(IV)–semidione complex B, which, in a strongly acidic reaction medium, may well be in equilibrium with its protonated form **2**. Subsequent addition of **2** to **3** would afford the Ti(IV)–azo radical cation complex C. It should be noted that both Cu(0) and Fe(II) do selectively reduce 3, even in the presence of a 10-fold excess of **1c**, to the corresponding acetphenones.[11]

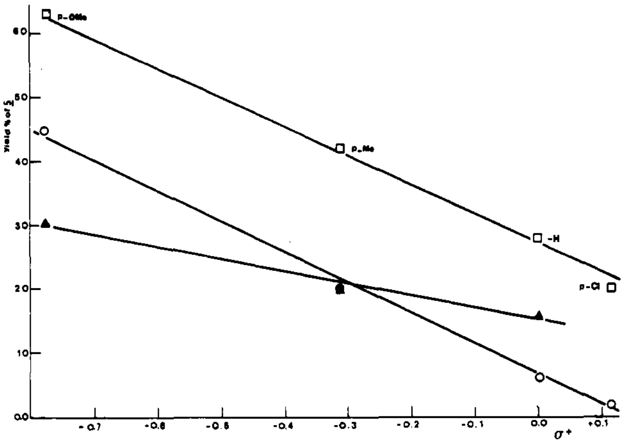


Figure 1. Plots of yields (%) of **5** vs σ^+ Hammett substituent constants (reaction performed at 20 °C with a $1/Ti^{3+}$ ratio of 1:3): **1a**, ○; **1b**, □; **1c**, ▲.

Formation of Monoacylhydrazines 6. The data in Table I show that the yield of **6** is more influenced by the natures of the groups R and R_1 of the α-dicarbonyl compound than by the nature of the para substituent of the diazonium ion. Moreover, for a given α-dicarbonyl compound (**1**), a high reaction temperature favors the formation of **6** over that of **4** (entries b, c, and f at 50 °C). Thus, 1,1-dibenzoylhydrazine (**4b**, 1 mol), when treated with aqueous acidic $TiCl_3$ (2 mL) and glacial acetic acid (15 mL) for 40 min, undergoes acid-catalyzed hydrolysis to form the monobenzoylhydrazine **6b**, in yields of 10 and 50% at 20 and 50 °C, respectively. Under the same conditions, the 1-acetyl-1-benzoylhydrazine (**4e**) gives the 1-benzoylhydrazine **6e** (30%) and the 1-acetylhydrazine **6′e** (20%) at 20 °C. At 50 °C, hydrolysis of **4e** is quantitative. Because in the hydrolysis of **4** acetyl is a better leaving group than benzoyl, the yield of **6** + **6′** increases and the yield of **4** decreases as the substrate goes from **1a** to **1b**. In the case of the biacetyl (**1c**), **4** was not detected because it was quantitatively hydrolyzed to **6i–k** under the reaction conditions.

Formation of Hydrazones 5 and 1,1-Diacyl-2-arylhydrazines 4. A Mechanistic Proposal. From the data

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[7] That the yields of recovered **1a** are 30 and 15% (entries a and b) and the yield of recovered **1b** is 21% (entry e) may well be consequences of electron transfer (eq 2). $E_{1/2}$ for substituted ArN_2^+ ions decrease in the order p-Cl, H, p-CH_3, p-OCH_3. In other words, when an electron-withdrawing substituent is present, the diazonium ion is more easily reduced.

[8] Meites, L. *Polarographic Techniques*, 2nd ed.; Interscience Publishers: New York, 1965; pp 683–4.

[9] Rogers, W.; Kipness, S. M. *Anal. Chem.* **1955**, *27*, 1916.

[10] This was found to be true in several cases. See ref 1 and (a) Clerici, A.; Porta, O. *J. Org. Chem.* **1985**, *50*, 76. (b) Clerici, A.; O. Porta; Arnone, A. *J. Org. Chem.* **1990**, *55*, 1240. (c) Kaim, W. *Acc. Chem. Res.* **1985**, *18*, 160. (d) Freudendenger, J. H., Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014.

[11] Citterio, A.; Serravalle, M.; Vismara, E. *Tetrahedron Lett.* **1982**, *23*, 1831.

in Table I it is clear that, for a given substrate **1**, the yield of **5** increases when the para substituent X on the phenyl ring of the diazonium ion is an electron-donating group. The correlations between the yield of **5** and the Hammett σ^+ values[12] of the substituents are shown in Figure 1 (for **1a**, $r = 0.999$; for **1b**, $r = 0.998$, and for **1c**, $r = 0.971$). Because the stoichiometry of the reaction requires that 4 equiv of Ti^{3+} be consumed for each mole of adduct **5** that is formed (entries d and h),[13] reduction of C to D and then of D to E, followed by dehydration of E,[14] appears to be a plausible route to **5** (Scheme III, path i).

At first glance, the substutuent effects that are observed[15] seem irreconcilable with the mechanism proposed. However, the two can, in fact, be reconciled by relating the yields of **5** to the contribution made by C to the resonance hybrid C ↔ G. In fact, there are two electronic configurations, C and G, possible for the nitrogen atoms of the azo radical cation. If Walter's theory,[16] i.e., that delocalization of an electron pair is favored over delocalization of an unpaired electron, is valid, the canonical form C, in which the odd electron is delocalized into the ring, would be the more stable of the two when electron-donating substituents are present. If, however, an electron-withdrawing group were present, the form G would be favored because conjugation of the nitrogen atom with the substituent would be possible. In such a case, the unpaired electron would tend to reside on the nitrogen atom. Thus the radical species would tend to be more reactive as the contribution of G to the resonance hybrid increases.

Such substituent effects have been observed in the dimerization of arylamino radicals to hydrazines[16] and of hydrazyl radicals to tetrazenes.[17] In both cases, the presence of an electron-donating substituent on the *N*-phenyl ring increases the stability of the radical, whereas the presence of an electron-withdrawing substituent reduces the radical's stability, thus rendering dimerization more probable. Two studies[18] have shown that the equilibrium constants for dissociation and recombination of the tetrazene ⇄ hydrazyl radical system can be correlated with the Hammett equation. ρ values of -1.52 and $+0.97$, respectively, were obtained. Recent ESR measurements[19] of the stability of hydrazyl radicals have confirmed that such substituent effects are operative.

In view of such evidence, it is not unreasonable to relate the yields of **5** and **4** to the extent to which the canonical forms C and G contribute to the resonance hybrid. The greater the contribution of C, the higher the stability of the azo radical cation. Thus, it may survive long enough to be reduced to the hydrazone **5** (Scheme III, path i). Conversely, when the contribution of G is large, the azo radical cation, a less stable and, hence, more reactive species, undergoes rapid cleavage of the more labile αC–βC σ bond (Scheme III, path ii) rather than reduction. Such C–C cleavage (β-scission),[20] which occurs within the coordination sphere of the Ti(IV) ion, leads, via the enolate form H, to a tightly organized transition state I in which both the acyl radical and the azo compound that are formed remain firmly bound to the metal ion. The acyl radical, which displays nucleophilic character,[21] then may add to the less electron-rich nitrogen atom N_1 of the N–N double bond. Such addition, which proceeds through a quasi-intramolecular six-membered transition state, would be favored. That a relatively stable 1,1-diacyl-2-arylhydrazyl radical (J) would be formed would also tend to further favor addition. The strong electron-withdrawing effect of the two carbonyl groups would effectively stabilize J, in which the unpaired electron resides on N_2.[19b] Reduction of J by a second equivalent of Ti^{3+} would give **4**. The stoichiometry is consistent with the observation that 2 equiv of Ti^{3+} are consumed for each mole of **4** that is formed. The high yields of **4** (and of **6** and **6′**) indicate that very little, if any, of the intermediates formed via β-scission escaped from the coordination sphere of the metal ion. Thus the mechanism is consistent with the substituent effects that are observed in the formation of **5** (Figure 1). That the mechanism is viable is also strongly supported by the good correlations shown in Figure 2, in which log [relative yield of the products derived from rearrangement (**4** + **6** + **6′**) divided by yield of product derived from direct reduction of the azo radical cation **5**] is plotted against the Hammett σ^+ values for the substituents (**1a**, $\rho = 1.49$, $r = 0.994$; **1b**, $\rho = 0.99$, $r = 0.999$; **1c**, $\rho = 0.45$, $r = 0.995$). These correlations reflect the contribution of G (relative to C) to the resonance hybrid. In other words, the rate of rearrangement of the azo radical cation increases, relative to the rate of reduction, as the electron-withdrawing power of the para substituent increases.

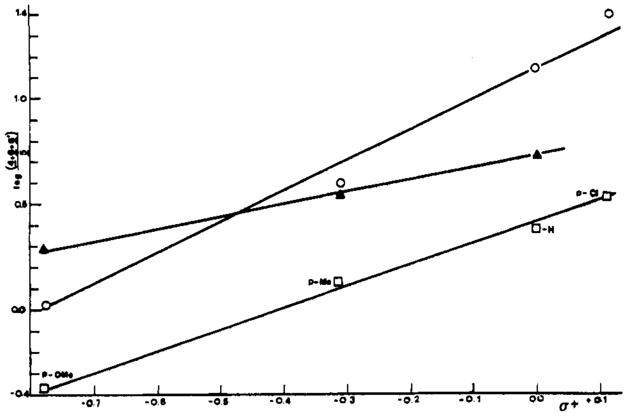

Figure 2. Plots of log (**4** + **6** + **6′**/**5**) vs σ^+ Hammett substituent constants (reaction performed at 20 °C with a $1/Ti^{3+}$ ratio of 1:3): **1a**, ○; **1b**, □; **1c**, ▲.

Although there is evidence[22] that acyl radicals add to azo compounds, the β-scission of an azo radical cation has, as far as is known, never been reported. Nevertheless, there is evidence[23] that suggests that, in aminium radical

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[12] Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

[13] That 25% of **1a** and 30% of **1b** (entries d and h) were recovered was due to the lack of sufficient Ti^{3+}.

[14] It is known that Ti^{4+} catalyzes the dehydration of benzylic and allylic alcohols to cations. See ref 10b and (a) Clerici, A.; Porta, O.; Zago, P. *Tetrahedron* **1986**, *42*, 566. (b) Reetz, M. T. *Organotitanium Reagents in Organic Chemistry*; Springer Verlag: Berlin, 1986; p 83. The dehydration of D (Scheme III) to a carbocation, followed by reduction, may well have eventually yielded **5**.

[15] The rate of reduction of the strong electrophilic radical cation C should be independent of the nature of the para substituent. Were this not so, the presence of an electron-withdrawing group would favor reduction, but not vice versa (see ref 7).

[16] (a) Walter, R. I. *J. Am. Chem. Soc.* **1966**, 88, 1923. (b) Walter, R. I. *J. Am. Chem. Soc.* **1966**, *88*, 1930.

[17] Goldsmidt, S.; Bader, J. *Annalen* **1929**, *473*, 137 and earlier papers.

[18] Wilmarth, W. K.; Schwartz, N. *J. Am. Chem. Soc.* **1965**, *77*, 4543 and 4551.

[19] (a) Forrester, A. R.; Hay, J. N.; Thompson, R. T. *Organic Chemistry of Stable Free Radicals*; Academic Press: London, 1968; p 137. (b) Forrester, A. R.; Hay, J. N.; Thompson, R. T., ref 19a, p 151.

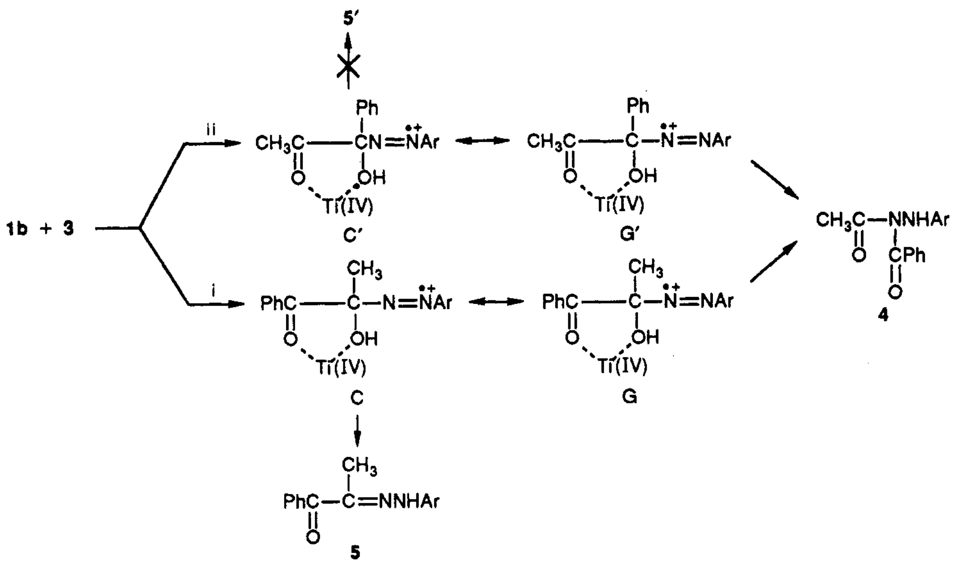
[20] We call such cleavage "β-scission" of an azo radical cation, by analogy with the well-known β-scission of alkoxyl radicals.

[21] Caronna, T.; Fronza, G.; Minisci, F.; Porta, O. *J. Chem. Soc., Perkin Trans. II* 1972, 1477.

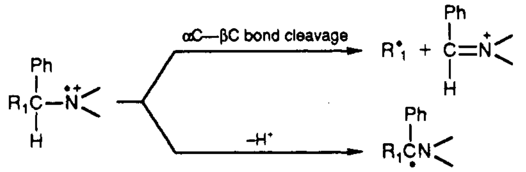
[22] (a) Kharasch, M. S.; Zimmerman, M.; Zimmt, W.; Nudenberg, W. *J. Org. Chem.* **1953**, *18*, 1045. (b) Horner, L.; Naumann, W. *Annalen* **1954**, *587*, 81. (c) Horner, L.; Naumann, W. *Annalen* **1954**, *587*, 93. (d) Mackay, D.; Marx, U. F.; Waters, W. A. *J. Chem. Soc.* **1964**, *64*, 4793.

[23] Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193–6299, and references cited therein.

Scheme IV



cations, the αC–βC bond is weak and, thus, cleavage of that bond is possible (eq 3). That the C–H bond of the carbon



(3)

(4)

α to the nitrogen of the aminium radical cation is weak has also been demonstrated.[23,24] So, depending upon the amino radical cation, deprotonation (eq 4) can compete with homolysis of the αC–βC bond.[24a] Analogously, in the reaction described here, when R = H (entries l and m),[25] G undergoes loss of the α-proton rather than αC–βC cleavage (Scheme III, path iii) and (phenylglyoxyl)hydrazine **7** is the only product that is isolated. It is possible that **7** could be formed by tautomerization of the unstable azo compound D (R_1 = H)[26] before the latter could be reduced. However, the presence of an electron-donating para substituent, which would increase the contribution of C to the resonance hybrid, leads to a complex mixture of unstable products.

How the products obtained from 1-phenyl-1,2-propanedione **1b** were formed is somewhat unclear because two different azo radical cations could have been intermediates (Scheme IV, C ↔ G and C′ ↔ G′). Either could have been formed, depending on whether electron transfer from the metal ion was to the acetyl or to the benzoyl group[1] (Scheme IV, path i and ii). Whereas hydrazone **5** would arise only by the reduction of C (no trace of **5′** was detected), it is impossible, at present, to establish if **4** was derived from G or from G′, via cleavage of the benzoyl or the acetyl group, respectively. The study of the reaction of other α-dicarbonyl compounds is now underway, with the aims of further elucidating the mechanism involved and extending the scope of the rearrangement which leads to 1,1-diacyl-2-arylhydrazines **4**, species which heretofore have not been described in the literature.[27]

Experimental Section

General Methods. The α-dicarbonyl compounds were commercially available research grade chemicals and were used as received. Arenediazonium tetrafluoroborates were prepared by standard procedures, of which the following is illustrative. An aqueous suspension of *p*-chloroaniline hydrochloride (prepared from *p*-chloroaniline (25 g), H_2O (78 mL), and concd HCl [40 mL]) was treated at 5 °C with a solution of $NaNO_2$ (15 g) in H_2O (27 mL). When diazotization was complete, a solution of $NaBF_4$ (28 g) in H_2O (50 mL) was added. The diazonium tetrafluoroborate that precipitated was washed thrice with H_2O, twice with EtOH, twice with Et_2O, and, finally, was dried in air. The solution of $TiCl_3$ (15% w/v, C. Erba) was standardized by titration against 0.1 N aqueous Ce(IV). ^1H NMR spectra of $CDCl_3$ solutions were recorded with a 250-MHz Brucker Model AC-250 instrument. Me_4Si served as an internal standard. IR spectra of mineral oil mulls were recorded with a Perkin-Elmer Model E-177 instrument. UV spectra of solutions in 95% EtOH were recorded with a JASCO Model Uvidec spectrophotometer. Mass spectra were recorded with a Hitachi-Perkin-Elmer Model RMU-6D spectrometer operated at 70 eV. Melting points (uncorrected) were measured with a Koffler apparatus. All reaction were monitored by thin layer chromatography on silica gel coated plates 60 F254 (Merck). Column chromatography was performed with Merck silica gel (0.04–0.063 mm).

General Procedures. To a well-stirred solution of **1** (10 mmol) and **3** (10 mmol) in glacial MeCOOH (150 mL) at rt (20 °C) was added 15% aqueous $TiCl_3$ (20 or 30 mmol) at once. A rapid color change, from blue to red-brown, accompanied the mixing of the reagents. The reaction mixture was stirred for 40 min; then it was poured into H_2O (150 mL) and the whole was extracted with EtOAc (3 × 300 mL). The combined extracts were carefully[28] washed with H_2O (3 × 150 mL), dried (Na_2SO_4), and concentrated in vacuo. A thick, reddish, solid residue was obtained. Flash chromatography of the residue on silica gel (hexane/EtOAc, from 9:1 to 6:4) usually gave, as a rule, **1**, **5**, **4**, **6**, benzoic acid, and **6′**, in that order. Table I gives isolated yields based on the starting material **1**.

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(24) (a) Lee, L. Y. C.; Ci, X.; Gianotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 175. (b) Lewis, F. D., Ho, I. I.; Simpson, J. T. *J. Am. Chem. Soc.* **1982**, *104*, 1924. (c) Inbar, S.; Linshitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048. (d) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586.

(25) With phenylglyoxal **1d**, Ti^{3+} transfers an electron solely to the aldehydic carbonyl group. See ref 1.

(26) Aliphatic azo compounds that bear a hydrogen on the carbon that is bonded to the azo group are unstable and tautomerize to hydrazones, which are, therefore, the reaction products. See: March, J. *Advanced Organic Chemistry*, 3rd ed.; J. Wiley and Sons: New York, 1985; p 533.

(27) Ionic acylation of 1-acyl-2-arylhydrazines takes place by attack of the acylium ion on the more electron-rich nitrogen atom and yields 1,2-diacyl-2-arylhydrazines. See: Patai, S. *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Interscience, J. Wiley and Sons: London, 1975; p 657.

(28) Extraction with EtOAc yields a Ti^{4+} salt that precipitates as a white crystalline solid upon concentration of the extract. The identity of this species is unknown. However, it is fairly soluble in water and has a certain lifetime before it is hydrolyzed to water-insoluble TiO_2.

1,1-Dibenzoyl-2-(*p*-chlorophenyl)hydrazine (4a): yellow crystals, mp 159–60 °C (Et_2O); IR[29] 3330 (NH), 1700, 1680, 1260 cm^{-1}; MS,[30] *m/e* 352, 350 ($M^{\bullet+}$), 230, 228 ($M^{\bullet+}$ – PhCOOH, m* 148.5), 217, 215, 105 (base peak), 77, 51; UV λ_{max} 205 (log ϵ 4.49), 243 nm (4.45); ^{1}H NMR δ 6.72 (2 H, m, Ph H), 6.8 (1 H, NH, s, D_2O-exchangeable), 7.22 (2 H, m, Ph H), 7.4 (4 H, m, Ph H), 7.52 (2 H, m, Ph H), 7.8 (4 H, m, Ph H). Anal. Calcd for $C_{20}H_{15}ClN_2O_2$: C, 68.46; H, 4.31; N, 7.99. Found: C, 68.41; H, 4.33; N, 7.89.

1,1-Dibenzoyl-2-phenylhydrazine (4b): pale yellow crystals, mp 166–7 °C (aqueous MeOH); IR[31] ν_{max} 3330, 3300 (NH), 1710, 1680, 1260 cm^{-1}; MS, *m/e* 316 ($M^{\bullet+}$), 194 ($M^{\bullet+}$ – PhCOOH, m* 119.1), 105 (base peak), 77, 51; UV λ_{max} 205 (log ϵ 4.42), 235 nm (4.39); ^{1}H NMR δ 6.80 (1 H, s, NH, D_2O-exchangeable), 7.0 (3 H, m, Ph H), 7.28 (2 H, m, Ph H), 7.40 (4 H, m, Ph H), 7.52 (2 H, m, Ph H), 7.86 (4 H, m, Ph H); ^{13}C NMR (CD_3COCD_3) δ 174.20 (s, 2 CO), 148.21 (s), 135.45 (s), 133.09 (d), 130.09 (d), 129.84 (d), 129.12 (d), 121.42 (d), 113.60 (d) (3 Ph). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.80; H, 5.15; N, 8.73.

1,1-Dibenzoyl-2-(*p*-tolyl)hydrazine (4c): yellow crystals, mp 139 °C (hexane/Et_2O, 1:1); IR ν_{max} 3340, 1690, 1250 cm^{-1}; MS, *m/e* 330 ($M^{\bullet+}$), 208 ($M^{\bullet+}$ – PhCOOH, m* 131.1), 105 (base peak), 77, 51; UV λ_{max} 205 (log ϵ 4.52), 235 nm (4.42); ^{1}H NMR δ 2.25 (3 H, CH_3, s); 6.75 (1 H, NH, s, D_2O-exchangeable), 6.9 (2 H, m, Ph H), 7.07 (2 H, m, Ph H), 7.35 (4 H, m, Ph H), 7.48 (2 H, m, Ph H), 7.82 (4 H, m, Ph H). Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.40; H, 5.40; N, 8.39.

1,1-Dibenzoyl-2-(*p*-anisyl)hydrazine (4d): yellow crystals, mp 138 °C (Et_2O); IR ν_{max} 3320, 1690, 1260, 1240 cm^{-1}; MS, *m/e* 346 ($M^{\bullet+}$), 224 ($M^{\bullet+}$ – PhCOOH, m* 145.02), 105 (base peak), 77, 51; UV λ_{max} 205 (log ϵ 4.48), 238 nm (4.43); ^{1}H NMR δ 3.73 (3 H, OCH_3, s), 6.72 (1 H, NH, s, D_2O-exchangeable), 6.83 (2 H, m, Ph H), 6.98 (2 H, m, Ph H), 7.4 (4 H, m, Ph H), 7.5 (2 H, m, Ph H), 7.82 (4 H, m, Ph H). Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.78; H, 5.17; N, 7.93.

Benzil mono(*p*-anisyl)hydrazone (5d): orange crystals, mp 125 °C (aqueous EtOH); IR[32] ν_{max} 3220, 1620, 1550, 1510, 1230 cm^{-1}; MS, *m/e* 330 ($M^{\bullet+}$), 122, 105 (base peak), 77, 51; ^{1}H NMR δ 3.75 (3 H, CH_3, s), 6.82 (2 H, m, Ph H), 6.96 (2 H, m, Ph H), 7.3–7.6 (8 H, m, Ph H), 8.05 (2 H, m, Ph H), 8.25 (1 H, NH, s, D_2O-exchangeable).

1-Acetyl-1-benzoyl-2-(*p*-chlorophenyl)hydrazine (4e): pale yellow crystals, mp 110–2 °C (hexane/EtOAc, 4:1); IR ν_{max} 3300, 1720, 1700, 1600, 1495, 1250 cm^{-1}; UV λ_{max} 205 (log ϵ 4.37), 240 nm (4.36); MS,[33] *m/e* 290, 288 ($M^{\bullet+}$), 274, 272, 248, 246 ($M^{\bullet+}$ – CH_2CO, m* 210), 105 (base peak), 77, 51; ^{1}H NMR δ 2.51 (3 H, CH_3, s), 6.72 (2 H, m, Ph H), 6.85 (1 H, NH, D_2O-exchangeable), 7.18 (2 H, m, Ph H), 7.38 (2 H, m, Ph H), 7.45 (1 H, m, Ph H), 7.68 (2 H, m, Ph H). Anal. Calcd for $C_{15}H_{13}ClN_2O_2$: C, 62.40; H, 4.54; N, 9.70. Found: C, 62.29; H, 4.47; N, 9.60.

1-Acetyl-1-benzoyl-2-phenylhydrazine (4f): pale yellow crystals, mp 129 °C (hexane/EtOAc, 1:1); IR ν_{max} 3320, 1715, 1675, 1600, 1500, 1250 cm^{-1}; UV λ_{max} 205 (log ϵ 4.29), 235 nm (4.29); MS,[33] *m/e* 254 ($M^{\bullet+}$), 212 ($M^{\bullet+}$ – CH_2CO, m* 176.9), 105 (base peak), 77, 65, 51, 43; ^{1}H NMR δ 2.51 (3 H, CH_3, s), 6.25 (1 H, NH, s, D_2O-exchangeable), 6.85 (2 H, m, Ph H), 6.95 (1 H, m, Ph H), 7.25 (2 H, m, Ph H), 7.4 (2 H, m, Ph H), 7.51 (1 H, m, Ph H), 7.72 (2 H, m, Ph H); ^{13}C NMR (CD_3COCD_3) δ 174.05 and 173.60 (s, 2 CO), 148.61 (s), 136.16 (s), 132.55 (d), 130.00 (d), 129.75 (d), 128.81 (d), 121.58 (d), and 135.60 (d, 2 Ph), 24.55 (q, CH_3). Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.80; H, 5.58; N, 10.96.

1-Acetyl-1-benzoyl-2-(*p*-tolyl)hydrazine (4g). All attempts to separate **4g** and **5g** were unsuccessful. The yield was determined by ^{1}H NMR analysis. **4g**: ^{1}H NMR δ 2.24 (3 H, s, CH_3), 2.51 (3 H, s, CH_3), 6.72 (2 H, m, Ph H), 6.78 (1 H, NH, s, D_2O-exchangeable), 7.3–7.5 (5 H, m, Ph H), 7.70 (2 H, m, Ph H); MS,[33] *m/e* 268 ($M^{\bullet+}$), 226 (M – CH_2CO, m* 190.6), 105 (base peak), 77, 51.

Propane-1,2-dione 1-phenyl-2-(*p*-tolyl)hydrazone (5g): yellow crystals, mp 160 °C (hexane/EtOAc, 9:1); IR ν_{max} 3290, 1625, 1250 cm^{-1}; MS, *m/e* 252 ($M^{\bullet+}$), 106, 105 (base peak), 77, 51; ^{1}H NMR δ 2.19 (3 H, CH_3, s), 2.28 (3 H, CH_3, s), 7.0 (2 H, m, Ph H), 7.1 (2 H, m, Ph H), 7.5 (3 H, m, Ph H), 7.88 (1 H, NH, s, D_2O-exchangeable), 7.95 (2 H, m, Ph H).

Propane-1,2-dione 1-phenyl-2-(*p*-anisyl)hydrazone (5h): yellow needles, mp 169–70 °C (hexane/EtOAc, 1:1); IR ν_{max} 3290 (NH), 1630 (CO); MS, *m/e* 268 ($M^{\bullet+}$), 122, 105 (base peak), 77, 51; ^{1}H NMR δ 2.2 (3 H, CH_3, s), 3.79 (3 H, OCH_3, s), 6.85 (2 H, m, Ph H), 7.02 (2 H, m, Ph H), 7.5 (3 H, m, Ph H), 7.9 (2 H, m, Ph H), 8.0 (1 H, NH, s, D_2O-exchangeable). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.50; H, 5.98; N, 10.36.

1-(Phenylglyoxyl)-2-(*p*-chlorophenyl)hydrazine (7l): yellow crystals, mp 181 °C (hexane/EtOAc, 1:1); IR ν_{max} 3300, 3200 (NH), 1680, 1660 (CO) cm^{-1}; MS,[34] *m/e* 276, 274 ($M^{\bullet+}$, base peak), 248, 246 ($M^{\bullet+}$ – CO, m* 220.8), 105, 77, 51; ^{1}H NMR δ 6.25 (1 H, NH, d, J = 6 Hz, D_2O-exchangeable) 6.82 (2 H, m, Ph H), 7.25 (2 H, m, Ph H), 7.50 (2 H, m, Ph H), 7.65 (1 H, m, Ph H), 8.30 (2 H, m, Ph H), 8.8 (1 H, NH, d, J = 6 Hz, D_2O-exchangeable). Anal. Calcd for $C_{14}H_{11}ClN_2O_2$: C, 61.21; H, 4.04; N, 10.20. Found: C, 61.15; H, 3.98; N, 10.01.

1-(Phenylglyoxyl)-2-phenylhydrazine (7m): yellow crystals, mp 125 °C (hexane/EtOAc, 1:1); IR ν_{max} 3320, 3220 (NH), 1680, 1655 (CO) cm^{-1}; MS,[34] *m/e* 240 ($M^{\bullet+}$), 212 ($M^{\bullet+}$ – CO, m* 187.2), 107, 106, 105 (base peak), 77, 51; ^{1}H NMR δ 6.3 (1 H, NH, d, J = 6 Hz, D_2O-exchangeable), 6.9 (3 H, m, Ph H), 7.22 (2 H, m, Ph H), 7.48 (2 H, m, Ph H), 7.62 (1 H, m, Ph H), 8.31 (2 H, m, Ph H), 8.85 (1 H, NH, d, J = 6 Hz, D_2O-exchangeable). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.83; H, 5.00; N, 11.58.

Acknowledgment. Partial financial support of this research from Ministero Pubblica Istruzione (MPI 60%) is gratefully acknowledged.

Supplementary Material Available: Spectroscopic data for, and literature references to, the known compounds **5b,c,e,f,i–k**, **6a–e**, and **6′e–h** (3 pages). Ordering information is given on any current masthead page.

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(29) In the spectrum of a mineral oil mull of **4a**, two bands, due to free and hydrogen-bonded C═O groups, appear in the C═O stretching region. The spectrum of a dilute $CHCl_3$ solution shows only one band, at 1700 cm^{-1}.

(30) The mass spectra of 1,1-dibenzoylhydrazines **4a–d** show prominent molecular peaks. The most characteristic feature of the fragmentation of these compounds on electron impact is the loss of benzoic acid from the molecular ions. The spectra show the presence of the appropriate metastable ions.

(31) In the spectrum of a mineral oil mull of **4b**, two bands appear in both the N—H and C═O stretching regions and are due to free and hydrogen-bonded amine and carbonyl groups, respectively. In the spectrum of a dilute $CHCl_3$ solution, only two bands, one each for N—H (3310 cm^{-1}) and C═O stretching (1690 cm^{-1}), are seen.

(32) The shift of the carbonyl band to 1620 cm^{-1} is attributed to the existence of **5c** and **5d** in their syn forms. These are stabilized by the formation of a hydrogen-bonded six-membered ring. See: El Kadem, H.; El Shafei, Z. H.; Hashem, M. M. *J. Chem. Soc. C* **1968**, 949.

(33) A characteristic feature of the fragmentation of 1-acetyl-1-benzoylhydrazines **4e–g** on electron impact is the loss of CH_2O. The mass spectra show the presence of the corresponding metastable ions.

(34) The fragmentation of **7l,m** on electron impact is characterized by the loss of CO from the molecular ions. The mass spectra show the presence of the corresponding metastable ions.