

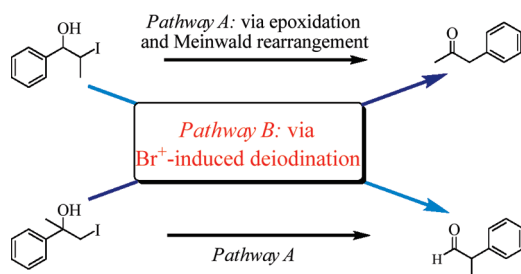
Halonium Ion-Assisted Deiodination of Styrene-Based Vicinal Iodohydrins Followed by Rearrangement through Phenyl Migration

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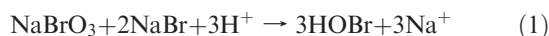


Acid activation of bromate/bromide couple at 0–10 °C was found to trigger the deiodination of styrene-based vicinal iodohydrins. Violet coloration of the organic layer was ascribed to formation of IBr. Deiodination was followed by phenyl migration and deprotonation leading to formation of phenyl acetone and 2-phenylpropanal in good yields from 1-iodo-2-phenylpropan-2-ol and 2-iodo-1-phenylpropan-1-ol, respectively. Phenyl acetaldehyde—which was obtained in 92% GC yield from styrene iodohydrin—was also presumably formed in analogous manner. NBS and HOCl too were effective for transformation of styrene iodohydrin into phenyl acetaldehyde.

Oxidizing agents such as *m*-CPBA are known to convert alkyl iodides into the corresponding alcohols in nonpolar solvent and even to olefins through *syn* elimination when strongly electron-attracting groups such as carbomethoxy or sulfonyl are present at α position.¹ There are also several reports in the literature on formation of hypervalent iodo

compounds with oxidizing agents,² including the formation of R-ICl₂^{2a} and R-I=O/R-IO₂^{2b} when RI is treated with chloronium or bromonium ion. We report here the observation of deiodination-cum-phenyl group migration when styrene-based iodohydrins were reacted with reagents bearing bromonium and chloronium ions.

When a stoichiometric amount of acid-activated BrO₃⁻/Br⁻ (1:2 molar ratio) (eq 1) was reacted with 2-bromo-1-phenylethanol, the solution gradually turned colorless, and bromomethylene phenyl ketone was obtained in 98% yield. In marked contrast, when a similar reaction was attempted with 2-iodo-1-phenylethanol, the solution turned violet in color and the product obtained was identified as phenyl acetaldehyde based on GC retention time and mass fragmentation pattern vis-à-vis standard sample (Supporting Information, entry 1, Table S1). Stirring was sufficient but not so vigorous as to mix up the two phases. The UV-vis absorption spectral profile of the product mixture matched that of IBr (prepared from I₂ and Br₂) (Figure 1),³ and the absorbance data indicated that all of the iodide from substrate and bromide from reagent were transformed into IBr at the end of the reaction. When the reaction was studied using a range of solvents, the maximum yield of phenyl acetaldehyde was obtained with 3:1 (v/v) ethylene dichloride (EDC)/water (Supporting Information, entry 1, Table S1) which was the initial solvent composition chosen.



Keeping the solvent composition fixed, and maintaining the temperature between 0 and 10 °C,⁴ the reaction with 2-iodo-1-phenylethanol was studied employing several different bromonium ion-generating reagents (Supporting Information, Table S2). The highest yield (92.1%) of phenyl acetaldehyde was obtained with 4:1 NaBrO₃/NaBr (entry 1, Table 1).⁵ HOCl also yielded the same product, albeit in lower (74.8%) yield, whereas the reaction failed with 1:2 IO₃⁻/I⁻ and I₂ (Supporting Information, entries 5 and 6, Table S2). The reaction with 4:1 BrO₃⁻/Br⁻ was extended to iodohydrins of other styrene derivatives (Table 1). Iodohydrins of the aromatic substituted styrene derivatives studied gave the corresponding phenyl acetaldehydes in 59–85% yields (entries 2–6, Table 1). The low yield in case of entry 3 was on account of appreciable formation of side products, while the low yield in the reaction of entry 4 was due to low conversion (see the GC-MS in the Supporting Information). Since phenyl acetaldehyde gave complex NMR spectra in CDCl₃, the above products were converted into their 2,4-DNP derivatives for characterization confirmation. The crystal structure was also obtained of the derivative of entry 2 (Supporting Information, Figure S1). Iodohydrins of styrene derivatives with side-chain substitution were also investigated

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(4) At room temperature, 2–3% of acetophenone was formed along with the phenyl acetaldehyde.

(5) Given that there is only 0.43 mol total of Br in this reagent per mole of iodine in substrate taken, all of the I from the substrate cannot be in the form of IBr in this case.

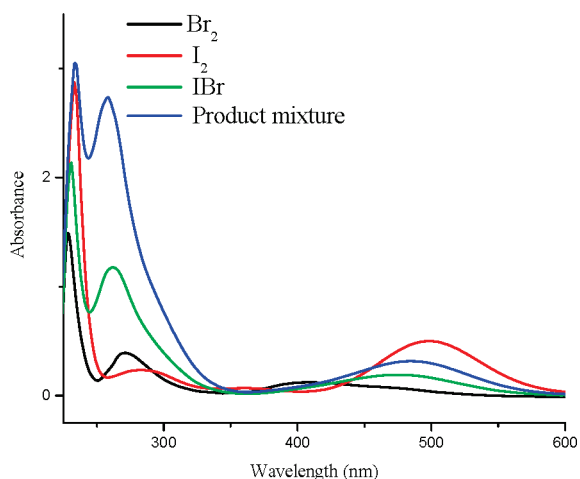


FIGURE 1. UV-vis spectra of 5.54×10^{-4} M I_2 , Br_2 , and IBr (prepared from I_2 and Br_2) in EDC and of diluted product mixture obtained from the reaction (in 25 mL of EDC) of 2-iodo-1-phenylethanol (5.54×10^{-3} mol) with acid-activated 1:2 BrO_3^-/Br^- (containing 5.54×10^{-3} mol of total Br). The organic layer was diluted 500 times with EDC prior to recording the spectrum.

(entries 7–10, Table 1). Cinnamic acid iodohydrin gave phenyl acetaldehyde in 74.7% yield under the optimized reaction conditions, while at room temperature, both phenyl acetaldehyde and acetophenone were formed in ca. 55% and 45% GC yields, respectively (Supporting Information). When the reaction was carried out with the iodohydrin of methyl cinnamate, methyl 3-oxo-3-phenylpropanoate was obtained as the sole product in 61.9% yield. 1-Iodo-2-phenylpropan-2-ol and 2-iodo-1-phenylpropan-1-ol gave phenylacetone and 2-phenylpropanal in 64% and 69% yields, respectively (entries 9 and 10, Table 1). Identities of both products were cross-checked by solving the crystal structures of their 2,4-DNP derivatives (Supporting Information, Figures S2 and S3). 2-Iodocyclohexanol was also subjected to reaction under the same conditions. The ring-contracted product, cyclopentanecarbaldehyde, was obtained in 21.7% yield. Iodohydrins of linear olefins (1-hexene; 1-octene) yielded only complex mixtures of products.

The results of entries 9 and 10 of Table 1 can be rationalized on the basis of bromonium ion-induced deiodination and accompanying phenyl group migration. With regard to the reactions of entries 1–6, these too may be explained through phenyl migration. Formation of phenyl acetaldehyde via epoxide formation and O-migration is, of course, the well-known pathway of the Meinwald rearrangement, which is less likely with the present methodology.^{6–8} The reaction of entry 7 must have also occurred through phenyl group migration since O-migration would have yielded phenylpyruvic acid instead. Deiodination and phenyl group

(6) GC-MS of the product mixtures of the reactions in Table 1 indicated traces of epoxide which may have formed as an impurity, presumably via a competing pathway.

(7) Meinwald, J.; Labana, S. S.; Chadha, M. S. *J. Am. Chem. Soc.* **1963**, *85*, 582.

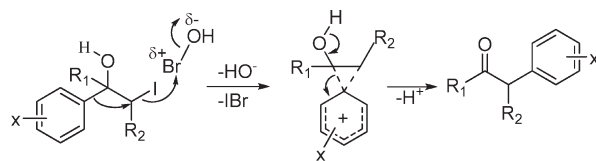
(8) (a) Sudha, R.; Narasimhan, K. M.; Saraswathy, V. G.; Sankaraman, S. *J. Org. Chem.* **1996**, *61*, 1877. (b) Kulasegaram, S.; Kulawiec, R. *J. Org. Chem.* **1997**, *62*, 6547. (c) Ranu, B. C.; Jana, U. *J. Org. Chem.* **1998**, *63*, 8212. (d) Robinson, M. W. C.; Pillinger, K. S.; Graham, A. E. *Tetrahedron Lett.* **2006**, *47*, 5919. (e) Miyamoto, K.; Okuro, K.; Ohta, H. *Tetrahedron Lett.* **2007**, *48*, 3255. (f) Tiffeneau, M. *Bull. Soc. Chim. Fr.* **1908**, *1*, 1205 and references cited therein.

TABLE 1. Reactions of Styrene-Based Iodohydrins with 4:1 BrO_3^-/Br^-

Entry	Substrate ^b	Time (h)	Conversion	Product ^c	Yield ^d (%)
1		3	100		92.1
2		3	100		80.7
3		3	100		59.1
4		3	67.3		67.3
5		3	80.4		74.2
6		3	90.3		85.1
7		6	100		74.7
8		6	61.9		61.9
9		2	100		64.0
10		3	100		69.0

^a $BR-O = 4:1 NaBrO_3/NaBr$; 0.43 mol total of Br taken per mole of substrate; 0.5 mol of H_2SO_4 taken per mole of substrate for all reactions; all reactions were carried out between 0 and 10 °C under gentle stirring. ^bSubstrate amount varied from 3 to 14 mmol. ^cProduct identity was initially assessed through analyses of mass fragmentation pattern in the GC-MS of the crude product mixture and later on through preparation of 2,4-DNP derivatives of all the compounds except those in entries 5, 7, and 8. ^dYield refers to GC area % recorded for crude product mixture after workup. Note that GC-MS of entries 4 and 8 showed only peaks due to starting material and product (Supporting Information), which is why the conversion and yield are identical in these cases.

SCHEME 1. Probable Reaction Pathway of the Bromonium Ion-Assisted Styrene-Based Iodohydrin Rearrangement



migration in the above cases may occur synchronously as shown in Scheme 1. Abstraction of I^- by Br^+ would yield IBr ,⁹ formation of which is evident from Figure 1. (Note, however, that IBr can also form from I_2 and Br_2 .) The

(9) Under the reaction conditions prevailing with 1:2 BrO_3^-/Br^- reagent, the reactive species is likely to be H_2OBr^+ resulting in a strongly electrophilic bromonium ion: Gilow, H. M.; Ridd, J. H. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1321. Rao, T. S.; Mali, S. I.; Damgat, V. T. *Tetrahedron* **1978**, *34*, 205. With 4:1 BrO_3^-/Br^- , still more reactive intermediates such as asymmetric Br_2O_2 are possible: Taube, H.; Dodgen, H. *J. Am. Chem. Soc.* **1949**, *71*, 3330 apart from the participation of IBr in the reaction.⁵

influence of substituents at the 2-position would be dictated by electronic effects such as inductive, π -donation (toward formation of nonclassical carbonium ion), and hyperconjugative stabilization effects.¹⁰ The effective π -donating ability of the phenyl substituent toward the stabilization of the carbocation intermediate may be responsible for the observed phenyl group migration in these cases. B3LYP/LACVP* energy calculation on the substrate of entry 1, Table 1, further suggests that the ground-state energy is lowest when the phenyl group is antiperiplanar to the leaving iodo group. This too would facilitate phenyl group migration.¹¹ H-Migration occurred to a small extent (2–3%) with styrene iodohydrin when the reaction temperature was raised from 10 °C to room temperature,⁴ whereas in the case of entry 7 the two pathways were equally facile at room temperature given the similar proportions of phenyl acet-aldehyde and acetophenone formed. The reaction of entry 8 provided the sole example in which the migratory aptitude of hydrogen was higher than that of the phenyl group.¹²

In conclusion, we have chanced upon an interesting reaction involving halonium ion-assisted electrophilic deiodination of styrene-based iodohydrins with accompanying phenyl group transfer at 0–10 °C, the reaction with the iodohydrin of methyl cinnamate being the only case where H-migration was preferred over phenyl migration. Although several reagents were effective, the best yields were obtained with acid-activated bromate/bromide (4:1 mol ratio) which is a source of reactive bromonium ion.

Experimental Section

General Procedure for Reaction of Iodohydrins with 4:1 BrO₃⁻/Br⁻ (Entry 1, Table 1). 2-Iodo-1-phenylethanol (744 mg, 3.0 mmol)¹³ and EDC (12 mL) were taken in a 50 mL round bottomed flask and stirred in water bath at 0–10 °C. To the above solution was added 177 mg of 4:1 NaBrO₃/NaBr [1.0 mmol NaBrO₃ + 0.25 mmol NaBr] in 2.0 mL of water followed by H₂SO₄ (1.5 mmol in 1 mL water) in one portion under gentle magnetic stirring, ensuring that the two phases were maintained separate (Schotten–Baumann condition). Stirring was continued for 3.0 h under the same conditions. The reaction mixture was diluted with water and extracted with CH₂Cl₂ (25 mL × 3). The combined organic layers were washed with aqueous Na₂S₂O₃. Finally, the layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to get crude product (92.1% yield by GCMS area %).

General Procedure for Preparation of the (2,4-Dinitrophenyl)-hydrazine Derivatives of Carbonyl Compounds Obtained from the Reactions of Iodohydrins with 4:1 BrO₃⁻/Br⁻ (Entry 1, Table 1). To the crude product obtained in the above step was added

(10) (a) Alem, K. V.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2002**, *106*, 10681. (b) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms and Structure*; Wiley: New York, 2007; Vol. 6, p 446.

(11) All geometries were fully optimized with the Becke3 Lee–Yang–Parr (B3LYP) method; Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. The reactions used the pseudopotential basis set LACVP*: Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. Vibrational analyses were also performed to confirm the local minima. All calculations were performed using Spartan'06 (Wavefunction, Inc.: Irvine, CA) quantum chemical program (Ganguly, B.; Kesharwani, M. K.; Agrawal, M. K.; Ghosh, P. K. Unpublished results).

(12) For the substrate of entry 8, Table 1, the ground-state energies of the two conformers, i.e., phenyl antiperiplanar to I and H antiperiplanar to I, were nearly equal, the former being lower by only 0.3 kcal/mol at the same level of theory.¹¹

(13) All the iodohydrins employed in the present work were synthesized and isolated following the literature procedure: Agrawal, M. K.; Adimurthy, S.; Ganguly, B.; Ghosh, P. K. *Tetrahedron* **2009**, *65*, 2791.

0.5 equiv of (2, 4-dinitrophenyl)hydrazine and dry THF until a clear solution was obtained. The reaction mixture was refluxed for 4 h employing a CaCl₂ guard tube. The reaction mixture was allowed to cool to room temperature, and methanol was added until turbidity was seen. This solution was allowed to chill at –15 °C and the precipitate filtered. The derivatives of the products of entries 2, 4, and 6 were recrystallized from CHCl₃/petroleum ether at room temperature, while those for entries 9 and 10 were recrystallized from THF/CCl₄. The dried solid was characterized using ¹H, ¹³C, IR, MS, DSC, and microanalysis (C, H, N) techniques. C, H, and N values indicate percent (w/w). Data for characterized compounds are provided below. Products of entries 5, 7, and 8 were identified on the basis of GC–MS of the crude product mixtures.

1-(2,4-Dinitrophenyl)-2-(2-phenylethylidene)hydrazine (Entry 1, Table 1). ¹H NMR (CDCl₃, 500 MHz) δ : 3.76 (d, J (H,H) = 5.0 Hz, 2H), 7.26–7.37 (m, 5H), 7.62 (d, J (H,H) = 5.5 Hz, 1H), 7.97 (d, J (H,H) = 9.5 Hz, 1H), 8.31 (d, J (H,H) = 9.5 Hz, 1H), 9.09 (s, 1H), 11.04 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ : 39.07, 116.6, 123.4, 127.2, 129.0, 130.0, 135.4 (*quat-C*), 137.9 (*quat-C*), 145.1 (*quat-C*), 148.7 (*quat-C*), 150.4 ppm. IR (KBr) ν_{\max} : 3293, 3101, 1618, 1592, 1332, 1306, 1262, 1215, 1139, 1075, 917, 841, 742, 700, 594 cm⁻¹. GCMS (70 eV) m/z : 300.10 [M⁺], obsd 323.61 [M⁺ + Na]. Anal. Calcd for C₁₄H₁₂N₄O₄: C, 56.00, H, 4.03; N, 18.67. Found: C, 57.04, H, 4.07; N, 17.16. Mp: 112–113 °C.

1-(2,4-Dinitrophenyl)-2-(2-*p*-tolylethylidene)hydrazine (Entry 2, Table 1). ¹H NMR (CDCl₃, 500 MHz) δ : 2.34 (s, 3H), 3.70 (s, 2H), 7.13–7.17 (m, 4H), 7.57 (t, J (H,H) = 5.5 Hz, 1H), 7.96 (d, J (H,H) = 9.5 Hz, 1H), 8.30 (dd, J (H,H) = 10.0 and J (H,H) = 2.5 Hz, 1H), 9.09 (d, J (H,H) = 1.0 Hz, 1H), 11.03 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ : 20.5, 38.1, 116.0, 122.9, 128.3, 129.1, 129.4, 131.7 (*quat-C*), 136.4 (*quat-C*), 137.4 (*quat-C*), 144.6 (*quat-C*), 148.5 (*quat-C*), 150.1. IR (KBr) ν_{\max} : 3278, 3055, 2919, 2358, 1614, 1513, 1425, 1327, 1129, 1066, 1043, 915, 811, 740, 561, 515 cm⁻¹. MS (70 eV) m/z : calcd 314.30 [M⁺], obsd 345.57 [M⁺ + Na]. Anal. Calcd for C₁₅H₁₄N₄O₄: C, 57.32; H, 4.49; N, 17.83. Found: C, 57.70; H, 4.46; N, 17.74. Mp: 148–149 °C.

1-(4-*tert*-Butylstyryl)-2-(2,4-dinitrophenyl)hydrazine (Entry 3, Table 1). ¹H NMR (CDCl₃, 500 MHz) δ : 1.37 (s, 9H), 2.22–2.58 (m, 1H), 3.73–3.75 (t, J (H,H) = 6.5 Hz), 7.57 (d, J (H,H) = 8.5 Hz, 2H), 8.05 (d, J (H,H) = 8.5 Hz, 2H), 8.11 (s, 1H), 8.28 (d, J (H,H) = 9.5 Hz, 2H), 9.16 (d, J (H,H) = 2.5 Hz, 1H), 15.61 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ : 30.5, 30.7 (*quat-C*), 116.7, 122.4 (*quat-C*), 125.7, 125.8, 125.9, 128.3, 129.2, 130.3, 133.1 (*quat-C*), 143.9 (*quat-C*), 158.1 (*quat-C*). IR (KBr) ν_{\max} : 3291, 3106, 3026, 2924, 1614, 1591, 1508, 1413, 1333, 1270, 1217, 1136, 1069, 1045, 790, 602, 470 cm⁻¹. MS (70 eV) m/z : calcd 356.32 [M⁺], obsd 356.63 [M⁺]. Anal. Calcd for C₁₈H₂₀N₄O₄: C, 60.66; H, 5.66; N, 15.72. Found: C, 57.57; H, 4.22; N, 14.72 (halogen-containing impurities in the product may have depressed the C, H, N values). Mp: 200–202 °C.

1-(2-(4-Bromophenyl)ethylidene)-2-(2,4-dinitrophenyl)hydrazine (Entry 4, Table 1). ¹H NMR (CDCl₃, 500 MHz) δ : 3.71 (d, J (H,H) = 3.5 Hz, 2H), 7.14 (d, J (H,H) = 7.0 Hz, 2H), 7.47 (d, J (H,H) = 7.0 Hz, 2H), 7.58 (s, 1H), 7.93 (d, J (H,H) = 9.0 Hz, 1H), 8.31 (d, J (H,H) = 8.5 Hz, 1H), 9.09 (s, 1H), 11.07 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ : 38.4, 116.5, 121.2 (*quat-C*), 123.4, 129.1 (*quat-C*), 130.0, 130.7, 132.0, 134.4 (*quat-C*), 138.1 (*quat-C*), 145.0 (*quat-C*), 149.3 ppm. IR (KBr) ν_{\max} : 3291, 3106, 3026, 2924, 1614, 1591, 1508, 1413, 1333, 1270, 1217, 1136, 1069, 1045, 790, 602, 470 cm⁻¹. (MS (70 eV) m/z : 377.99 [M⁺]/379.99 [M⁺ + 2], obsd 401.46 [M⁺ + Na]/403.46 [M⁺ + 2 + Na]). Anal. Calcd for C₁₄H₁₁BrN₄O₄: C, 44.52; H, 2.92; N, 14.78. Found: C, 44.18; H, 2.57; N, 14.44. Mp: 153–154 °C.

1-(2-(4-(Chloromethyl)phenyl)ethylidene)-2-(2,4-dinitrophenyl)-hydrazine (Entry 6, Table 1). ¹H NMR (CDCl₃, 500 MHz) δ : 3.76

(d, $J(\text{H,H}) = 5.5$ Hz, 2H), 4.58 (s, 2H), 7.26–7.40 (m, 4H), 7.59 (t, $J(\text{H,H}) = 5.5$ Hz, 1H), 7.95 (d, $J(\text{H,H}) = 9.5$ Hz, 1H), 8.31 (dd, $J_1(\text{H,H}) = 2.5$ and $J_2(\text{H,H}) = 9.5$ Hz, 1H), 9.08 (d, $J(\text{H,H}) = 2.5$ Hz, 1H), 11.05 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 38.2, 45.3, 116.0, 122.9 (*quat-C*), 127.8 (*quat-C*), 128.5, 128.7, 128.8, 128.9, 129.5, 135.2 (*quat-C*), 144.5 (*quat-C*), 149.3. IR (KBr) ν_{max} : 3299, 3095, 2925, 2856, 1618, 1592, 1423, 1332, 1311, 1266, 1133, 1076, 832, 741, 720, 679, 593, 508 cm^{-1} . MS (70 eV) m/z : calcd 348.06 [M^+]/350.08 [$\text{M}^+ + 2$], obsd 347.62 [M^+]/349.60 [$\text{M}^+ + 2$]. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{ClN}_4\text{O}_4$: C, 51.66; H, 3.76; N, 16.07. Found: C, 51.73; H, 3.79; N, 15.98. Mp: 116–130 °C.

1-(2,4-Dinitrophenyl)-2-(1-phenylpropan-2-ylidene)hydrazine (Entry 9, Table 1). ^1H NMR (CDCl_3 , 500 MHz) δ : 2.00 (s, 3H), 2.73 (s, 2H), 7.25–7.36 (m, 5H), 8.00 (d, $J(\text{H,H}) = 9.5$ Hz, 1H), 8.31 (dd, $J_1(\text{H,H}) = 2.5$ and $J_2(\text{H,H}) = 9.5$ Hz, 1H), 9.12 (d, $J(\text{H,H}) = 2.5$ Hz, 1H), 11.05 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 14.9, 44.9, 116.0, 122.9 (*quat-C*), 126.6, 128.3, 128.5, 129.5, 135.6 (*quat-C*), 137.3 (*quat-C*), 144.7 (*quat-C*), 156.1 (*quat-C*). IR (KBr) ν_{max} : 3299, 3095, 2925, 2856, 1618, 1592, 1423, 1332, 1311, 1266, 1133, 1076, 832, 741, 720, 679, 593, 508 cm^{-1} . MS (70 eV) m/z : calcd 314.10 [M^+], obsd 315.55 [$\text{M}^+ + \text{H}^+$]. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_4$: C, 57.32; H, 4.49; N, 17.83. Found: C, 56.77; H, 4.50; N, 17.44. Mp: 144–145 °C.

1-(2,4-Dinitrophenyl)-2-(2-phenylpropylidene)hydrazine (Entry 10, Table 1). ^1H NMR (CDCl_3 , 500 MHz) δ : 1.58 (d, $J(\text{H,H}) = 7.0$ Hz, 3H), 3.85 (q, $J(\text{H,H}) = 5.5$ Hz, 1H), 7.26–7.60 (m, 6H), 7.97 (d, $J(\text{H,H}) = 9.5$ Hz, 1H) 8.31 (d, $J(\text{H,H}) = 7.5$ Hz, 1H), 9.10 (s, 1H), 11.02 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ :

18.0, 42.5, 116.1, 122.9 (*quat-C*), 126.8, 127.0, 128.5, 129.5, 140.7 (*quat-C*), 144.7 (*quat-C*), 153.8. IR (KBr) ν_{max} : 3291, 3069, 2931, 2887, 1615, 1515, 1451, 1424, 1326, 1220, 1129, 1090, 1018, 914, 836, 763, 699, 545, 516 cm^{-1} . MS (70 eV) m/z : calcd 314.10 [M^+], obsd 337.57 [$\text{M}^+ + \text{Na}$]. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_4$: C, 57.32; H, 4.49; N, 17.83. Found: C, 57.26; H, 4.21; N, 17.73. Mp: 116–118 °C.

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Supporting Information Available: Solvent and reagent optimization; GC–MS of crude products; ^1H and ^{13}C NMR spectra; and combined crystallographic information files in CIF format for 2,4-DNP derivatives of compounds of entries 2, 9, and 10, Table 1, with CCDC nos. CCDC-739028, CCDC-738835, and CCDC-738836, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.