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Alkyl Nitrate Nitration of Active Methylene Compounds. Nitration of Arylidene and of Alkylidene Phenylhydrazines[1]

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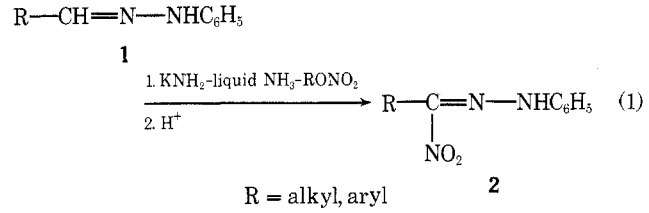
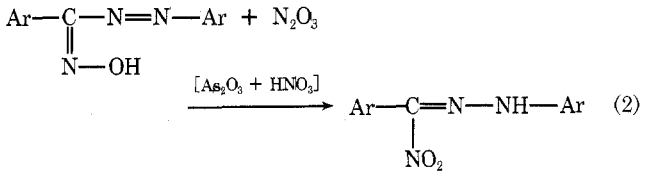
The alkyl nitrate nitration of arylidene and alkylidene phenylhydrazines affords the corresponding α-nitroarylidene and α-nitroalkylidene phenylhydrazines. Exclusive nitration on carbon is observed. This is in contrast to alkylation and acylation reactions which occur on nitrogen. The NMR spectra of the nitro compounds show the presence of both the *Z* and *E* isomers. The ratio of the isomers varies with the polarity of the solvent, the *Z* configuration predominating in nonpolar media owing to intramolecular hydrogen bonding.

In continuation[2] of our studies of the alkyl nitration, we are now reporting on its application to the synthesis of α-nitroarylidene and α-nitroalkylidene phenylhydrazines (eq 1).



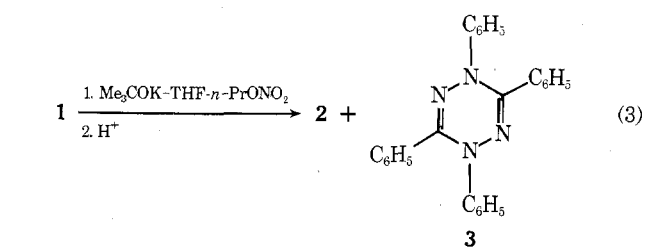
(1)

Previously, the only available method for preparing these compounds involved the coupling of diazonium compounds with salts of primary nitro compounds.[3,4] The method has afforded moderate yields and suffered because substituted arylnitromethanes are not readily available. α-Nitroarylidene phenylhydrazines have also been obtained in low yields from the oxidation of arylazoaldoximes[5] (eq 2).



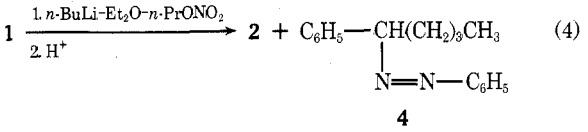
(2)

The nitration reaction in eq 1 was studied in several base–solvent systems with 1 (R = C_6H_5) as the model compound; the results are summarized in Table I. Highest yields (91%) of α-nitrobenzylidene phenylhydrazine (**2**) (R = C_6H_5) were obtained in the potassium amide–liquid ammonia system when the molar ratio of 1 to base to nitrating agent was 1:1:2. In the potassium *tert*-butoxide–tetrahydrofuran (THF) system, the yield of **2** was 80% but the reaction was accompanied by the formation of 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine (**3**) (eq 3). It is very likely that **2** is the precursor in the formation of **3** for **2** was converted into **3** on heating in ethanolic potassium hydroxide or methanolic sodium methoxide.[6]



(3)

When the nitration of **1** was carried out in the *n*-butyllithium–ethyl ether system, 1-phenylazo-1-phenylpentane (**4**) was the major product (40%) and **2** the minor product (30%) (eq 4). Compound **4** arose from a nucleophilic attack of *n*-butyllithium on the azomethine carbon of **1**, followed by air oxidation, a reaction which is well documented.[7]



(4)

The generality of the reaction in the potassium amide–liquid ammonia system was established by its application to a variety of compounds **1** including those derived from heterocyclic carboxaldehydes. As indicated by the data shown in Table II, the yields of some of the nitro compounds were substantially higher when reactions were carried out in a more concentrated medium. For instance, the yield of α-nitroethylidene phenylhydrazine (**5**) was increased by 53% when the concentration of potassium amide was increased from 0.3 to 0.7 M. This phenomenon was previously observed in the nitration of alkylsulfonate esters[8] and alkyl-substituted heterocyclics.[9]

However, nitrations in a more concentrated medium did not improve the yields of α-nitro-1-naphthylidene phenylhydrazine and α-nitro-3-picolylidene phenylhydrazine.

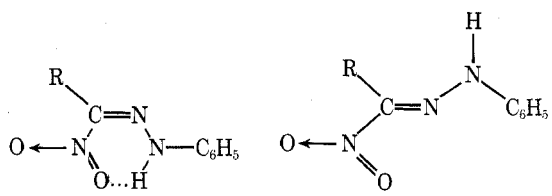
The low yields of compounds **2** (R = alkyl), with the exception of compound **5**, are very likely due to the instability of the starting materials.

Spectra of Compounds 2. A detailed study of the NMR spectra of compounds **2** indicated that in solution, both *E* and *Z* isomers were present. In relatively nonpolar solvents, the *Z* isomer predominated. This can be explained on the basis of its increased stability due to intramolecular hydrogen bonding. For example, the spectrum of **2** (R = C_6H_5) in $CDCl_3$ showed two NH absorptions at δ 12.0 and 8.0, which integrated to a value of 0.7 and 0.3 protons, respectively. The signals at δ 12.0 and 8.0 were assigned to the *Z* and *E* isomers, respectively. In a recent NMR study of these compounds, the authors reported only one NH signal in $CDCl_3$ at δ 11.73–11.89 and assigned it to the *Z* isomer.[10] The absorption peak at 12.0

Table I. Effect of Various Base–Solvent Systems on the Nitration of Benzylidene Phenylhydrazine [a] (1, R = C_6H_5)

Base–solvent	α-Nitrobenzylidene phenylhydrazine yield, %	Recovered 1 yield, %
KNH_2–liquid NH_3	91	3
$NaNH_2$–liquid NH_3	45[b]	45
$LiNH_2$–liquid NH_3	2	90
$(CH_3)_3COK$–THF	80	c
n-BuLi–Et_2O	33	21[d]

[a] In all experiments the molar ratio of 1 to base to n-propyl nitrate was maintained at 1.0:1.0:2.0 in approximately 300 ml of solvent. [b] When the molar ratio of 1 to sodium amide was 1.0:2.0, the yield of 2 was unchanged. [c] A 20% yield of 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine (3) was isolated. [d] A 40% yield of 1-phenyl-1-phenylazopentane (4) was obtained.



Z isomer E isomer

R = H, alkyl, aryl

ppm corresponds very closely to the NH absorptions observed by Karabatsos in the o-nitrophenylhydrazine derivatives of several aldehydes and ketones where intramolecular hydrogen bonding was evident.[11]

In Me_2SO-d_6 the equilibrium of the Z and E isomers in 2 (R = C_6H_5) was found to be in favor of the latter. The NH signal at δ 12.0 now integrated to 0.3 protons while that of the E isomer was shifted downfield from δ 8.0 to δ 10.50 and integrated to 0.7 protons. Apparently, the shift in the equilibrium to the thermodynamically more stable E isomer was favored by the intermolecular hydrogen bonding between the NH and the solvent. Similarly in 2 (R = alkyl) the equilibrium was in favor of the Z isomer in $CDCl_3$ and of the E isomer in Me_2SO-d_6.

Evidence for the rapid interconversion of the E and Z isomers in these nitro compounds was found when the spectrum of 2 (R = C_6H_5) was investigated at various temperatures. When a Me_2SO-d_6 solution of 2 was heated to 55 °C, the two NH signals at δ 12.0 and 10.51 coalesced into a single broad absorption between δ 12.0 and 10.5.[12] At this temperature integration of the spectrum over the range of δ 10.5–12.0 resulted in a constant value of one proton. On cooling the solution to 40 °C, the two NH signals reappeared at δ 12.0 and 10.51 which integrated to 0.3 and 0.70 protons, respectively.

The extended conjugation in these compounds was indicated in their infrared spectra by the absorption of the azomethine linkage at 1560–1580 cm^{-1} and of the nitro group at 1500 and 1300 cm^{-1}. In compounds 1, the azomethine absorption occurred near 1600 cm^{-1}. Unconjugated nitro groups usually absorb at 1550 and 1350 cm^{-1}.

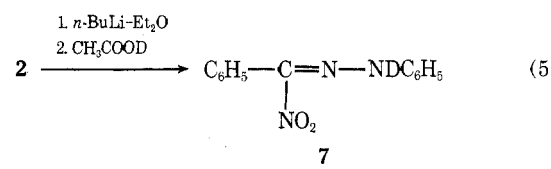
The mass spectra of compounds 2 showed molecular ions as well as the preferential loss of nitrous acid rather than of the nitro group. In each case, the synchronous loss of nitrous acid was accompanied by the presence of a metastable ion. It was established that the loss of nitrous acid involved the amino hydrogen for the mass spectrum of N-deuterio-α-nitrobenzylidene phenylhydrazine (7) showed the loss of deuterated nitrous acid which again was accompanied by the presence of a metastable ion. Compound 7 was prepared by

Table II. Preparation of $RC(NO_2)$=N–NHC_6H_5 [a,b]

R	Yield, %[c]	Mp, °C
2-$MeOC_6H_4$	28 (65)[d]	120–125
4-$MeOC_6H_4$	74	112–113
2-MeC_6H_4	70	98–100
4-MeC_6H_4	94	118–120
2-ClC_6H_4	21 (45)[d]	124–126
4-ClC_6H_4	73	127.5–129
4-BrC_6H_4	16 (58)[d]	125–126 dec
4-$Me_2CHC_6H_4$	94	103–104
4-$CF_3C_6H_4$	83	127.5–130 dec
1-Naphthyl	14 (14)[d]	124–126
2-Naphthyl	46	129–131
2-Furyl	19 (47)[d]	110–111
2-Thienyl	83	124–126.5 dec
3-Pyridyl	38	117–119
H	70	98–100
Me	30 (83)[d]	142–144
Pr	30 (15)[d]	63–65

[a] Satisfactory analytical data were reported for all new compounds listed in this table. [b] Unless otherwise noted, the nitrations were carried out at −33 °C in ca. 0.3 M solution of potassium amide. The nitro compounds were obtained upon aqueous acidification of their crude nitronate salts with acetic acid. Recrystallizations were carried out with 95% ethanol. [c] Yields are based on starting materials. [d] Nitrations were performed at −33 °C in ca. 0.7 M solution of potassium amide.

treating 2 (R = C_6H_5) with n-butyllithium followed by the addition of deuterated acetic acid (eq 5).



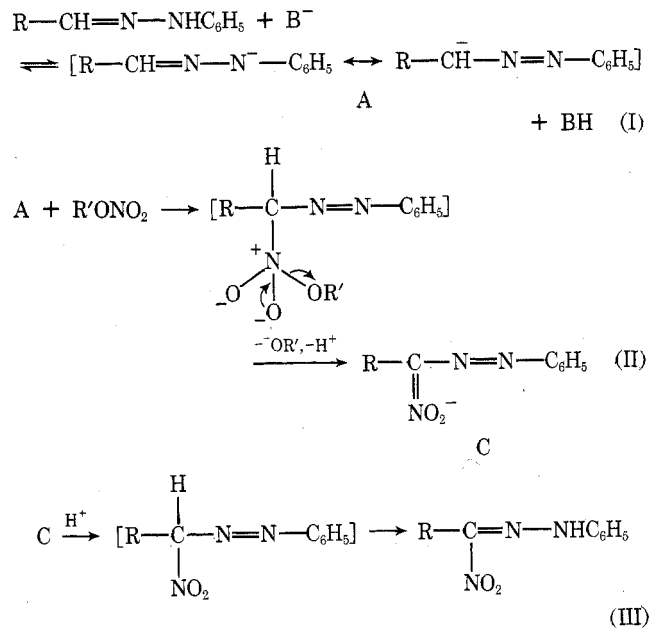
(5)

7

Discussion

This investigation has shown that the alkyl nitration of compounds 1 affords only C-nitro compounds. The formation of these products can be envisioned by the mechanism shown in Scheme I. The initial reaction involves proton abstraction

Scheme I



(I)

(II)

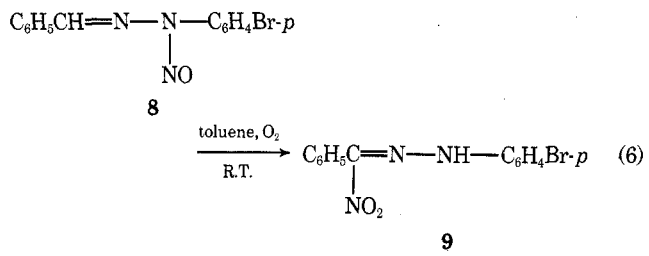
(III)

(step I) with the formation of a resonance stabilized ambident anion. The remaining steps have been discussed previously.[2]

The exclusive formation of *C*-nitro compounds might be a consequence of the greater nucleophilicity of the carbanion over the anilide ion (step II). Moreover, a nitroamino compound resulting from an electrophilic attack of nitrate ester on nitrogen would probably revert to starting material because it could not be stabilized by salt formation.

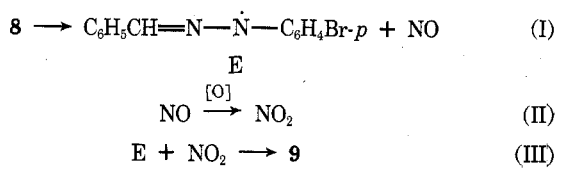
Exclusive attack on carbon has also been observed in nitrosations of compounds **1** with alkyl nitrites under alkaline conditions.[5] Subsequently, the nitroso compounds tautomerized to the corresponding oximes. On the other hand nitrosations of compounds **1** (R = C_6H_5) under acidic conditions have afforded *N*-nitrosoarylidene phenylhydrazines which, in base, rearranged to their isomeric arylazoaldoximes.[13]

In order to establish that such rearrangement was not involved in the formation of **2** (R = C_6H_5) during the alkyl nitrate nitration, attempts were made to prepare a *N*-nitroarylidene phenylhydrazine. When a dry toluene solution of *N*-nitrosobenzylidene 4-bromophenylhydrazine[13] (**8**) was subjected to a stream of oxygen at room temperature, instead of the nitramine there was obtained a 45% yield of α-nitrobenzylidene 4-bromophenylhydrazine[4] (**9**) (eq 6). The

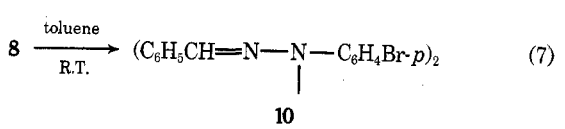


transformation might occur by the pathway shown in Scheme II. In step I, **8** dissociates into the resonance stabilized radical

Scheme II



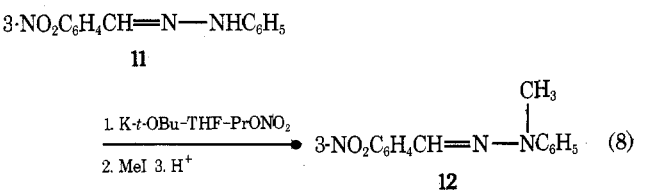
E and nitric oxide which is oxidized to nitrogen dioxide in step II. Combination of the latter with E in step III then affords **9**.[14] Some evidence of step I was obtained when, in the absence of oxygen, a toluene solution of **8** kept at room temperature for 24 h afforded a 12% yield of 1,4-dibenzal-2,3-di(*p*-bromophenyl)tetrazabutane (**10**) (84% of **8** was recovered) (eq 7).



Compound **10** was also formed when **8** was kept for 3 weeks in a vacuum desiccator. The mass spectrum of **10** gave molecular ions at *m/e* 548, 546, and 544 in a ratio of 1:2:1 which indicated the presence of two bromine atoms.

The instability of *N*-nitrosobenzylidene phenylhydrazine has already been noticed by Busch and Kunder[13] who reported that on standing the compound was converted to 1,4-dibenzal-2,3-diphenyltetrazabutane.

The exclusive substitution on carbon in the alkyl nitration and nitrosation of compounds **1** is in contrast to alkylation reactions which in alkaline media lead to exclusive substitution on nitrogen.[15] Apparently these reactions are less influenced by the nucleophilicity of the anion. This conclusion was further substantiated by experiments in which certain compounds **1** did not undergo the alkyl nitration but readily underwent alkylation. For example, 3-nitrobenzylidene phenylhydrazine (**11**) was recovered unchanged from nitrations in the potassium amide–liquid ammonia or potassium *tert*-butoxide–THF system. However, when methyl iodide was added to the reaction mixture, a quantitative yield of 3-nitrobenzylidene *N*-methylphenylhydrazine[16] (**12**) was obtained (eq 8).



Experimental Section

Apparatus. Nitrations were performed in a thoroughly dried 500-ml four-necked flask equipped with a dry ice condenser, mechanical stirrer, thermometer, and pressure equalizing dropping funnel.

α-Nitrobenzylidene Phenylhydrazine (2, R = C_6H_5). A. Employing Potassium Amide in Liquid Ammonia. The following experiment is typical of the procedure employed in the potassium amide–liquid ammonia system. To a freshly prepared solution of potassium amide (0.075 mol) in 300 ml of ammonia was added 14.7 g (0.075 mol) of benzylidene phenylhydrazine (**1**, R = C_6H_5) rapidly at −33 °C. After stirring for 45 min, 15.75 g (0.15 mol) of *n*-propyl nitrate was added as rapidly as possible while the temperature was kept at −33 °C.[17] The solution was stirred for an additional 30 min, the ammonia gradually replaced with absolute ether, and the reaction mixture filtered after room temperature was reached (3–4 h).

The crude potassium phenylazophenylmethanenitronate was dried in vacuo, dissolved in 300 ml of water, filtered, and acidified to pH 6 with glacial acetic acid at room temperature. Filtering and washing with water afforded 16.3 g (91%) of α-nitrobenzylidene phenylhydrazine as red-orange plates (95% C_2H_5OH): mp 103–104 °C (lit.[5] mp 102–103 °C); uv max (95% C_2H_5OH) 403 nm (log ε 3.89); NMR ($CDCl_3$) δ 7.0–7.8 (m, 10, ring H), 8.0 (s, 0.3, NH), and 12.0 (s, 0.7, NH); ir (KBr) 3226 (NH), 1567 (C=N), and 1502 and 1304 cm^{-1} (NO_2); mass spectrum (75 eV) *m/e* (rel intensity) 241 (36.1), 195 (20.7), and 194 (100.0).

Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.61; H, 4.59; N, 17.54.

The ethereal filtrate was concentrated in vacuo to give 2.2 g (15%) of **1** (R = C_6H_5), mp 154–156 °C (lit.[18] mp 156 °C).

B. Employing Potassium *tert*-Butoxide in THF. To a suspension of sublimed potassium *t*ert-butoxide (0.075 mol) in 250 ml of dry THF was added 14.7 g (0.075 mol) of **1** (R = C_6H_5) at −50 °C under nitrogen. After stirring for 45 min, 15.75 g (0.15 mol) of *n*-propyl nitrate was added rapidly at −30 °C. Stirring was continued for 30 min at −30 °C, and the solution was warmed to −10 °C and acidified with 9.0 g (0.15 mol) of glacial acetic acid dissolved in 10 ml of THF. The suspension was warmed to room temperature and filtered, the ethereal layer concentrated in vacuo, and the residue refluxed in 200 ml of 95% ethanol. Filtration gave 0.75 g (20%) of 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine (**3**): mp 203–205 °C (lit.[6] mp 203–204 °C); ir (KBr) 1600 cm^{-1} (C=N); NMR ($CDCl_3$) δ 6.9–7.5 (m, ring H).

The ethanolic solution was cooled to afford 14.5 g (80%) of **2** (R = C_6H_5), mp 103–104 °C.

C. Employing *n*-Butyllithium in Absolute Ether. To a solution of *n*-butyllithium (0.05 mol in 20 ml of hexane) in 100 ml of absolute ether was added 9.8 g (0.05 mol) of **1** (R = C_6H_5) at 5 °C under nitrogen. The solution was stirred for 45 min and cooled to −70 °C, and 10.5 g (0.10 mol) of *n*-propyl nitrate was rapidly added. The reaction mixture was warmed to 0 °C and poured into 300 ml of water, and the ethereal layer separated. The aqueous layer was acidified with glacial acetic acid and filtered to give 4.0 g (33%) of **2** (R = C_6H_5), mp 103–104 °C.

The ethereal solution was concentrated in vacuo to give a semisolid. Addition of *n*-hexane followed by filtration gave 2.0 g (21%) of **1** (R = C_6H_5), mp 154–156 °C, mass spectrum (75 eV) *m/e* 196.

The hexane solution was evaporated in vacuo to give 4.6 g (40%) of 1-phenylazo-1-phenylpentane (4): bp 120 °C (0.15 mm); ir (neat) 1600 cm^{-1} (N=N); NMR ($CDCl_3$) δ 0.8 (t, 3, CH_3CH_2), 1.0–2.0 (m, 4, CH_2CH_2), 2.1 (m, 2, CH_2), 4.6 (t, 1, $CHCH_2$), and 6.6–7.8 (m, 10, ring H); mass spectrum (75 eV) m/e 252.

α-Nitrobenzylidene 4-Bromophenylhydrazine (9). A. Employing N-Nitrosobenzylidene 4-Bromophenylhydrazine (8). To 100 ml of oxygen-free toluene was added 0.5 g (1.6 mmol) of N-nitrosobenzylidene 4-bromophenylhydrazine[13] at room temperature with stirring. Oxygen was then introduced to the solution via a balloon. Stirring was continued for 24 h at room temperature and then the solution was concentrated in vacuo. The orange solid was recrystallized from petroleum ether (bp 30–60 °C) to give 0.25 g (45%) of α-nitrobenzylidine 4-bromophenylhydrazine (9): mp 127–128 °C (lit.[4] mp 128 °C); ir (KBr) 3250 (NH), 1570 (C=N), and 1490 and 1300 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 7.0–7.7 (m, 9, ring H) and 11.9 (s, 1, NH).

B. Employing Compound 2 (R = C_6H_5). To a solution of 3.0 g (0.012 mol) of 2 in 15 ml of glacial acetic acid was added dropwise at room temperature 3.0 g (0.018 mol) of bromine. Addition of 25 ml of water gave a red precipitate. Recrystallization from 95% ethanol afforded 3.5 g (87%) of 9, mp 128 °C.

1,4-Dibenzal-2,3-di(4-bromophenyl)tetrazabutane (10). To 100 ml of oxygen-free toluene was added with stirring 0.5 g (1.6 mmol) of compound 8 at room temperature. Stirring was continued for 24 h and then the reaction vessel was opened to the atmosphere. Oxides of nitrogen were detected by a positive potassium iodide–starch paper test. Concentration of the reaction mixture in vacuo gave a yellow oil. Addition of 20 ml of a 1:1 mixture of ether–petroleum ether (bp 30–60 °C) to the oil gave a precipitate. Filtration afforded 0.05 g (12%) of 1,4-dibenzal-2,3-di(4-bromophenyl)tetrazabutane:[13] mp 170–175 °C; ir (KBr) 1590 cm^{-1} (C=N); NMR (Me_2SO-d_6) δ 7.0–8.0 (m, ring H and CH); mass spectrum (75 eV) m/e (rel intensity) 548 (31.6), 546 (63.0), 54.4 (31.6), 378 (41.5), 376 (41.5), 171 (100.0), and 169 (100.0).

The filtrate was concentrated in vacuo to give 0.42 g (84%) of recovered 8: mp 68 °C (lit.[13] mp 68–69 °C); ir (KBr) 1447 cm^{-1} (N–N=O).

***N*-Deuterio-α-nitrobenzylidene Phenylhydrazine (7).** To 0.01 mol of n-butyllithium dissolved in 20 ml of n-hexane was added 2.41 g (0.01 mol) of compound 2 (R = C_6H_5) with stirring at −20 °C under nitrogen. Stirring was continued for 30 min at 0 °C and then 1.0 g (0.016 mol) of deuterated acetic acid was added dropwise. The suspension was filtered at room temperature and dried ($MgSO_4$), and the solvent was removed in vacuo. Recrystallization of the residue from n-hexane gave 2.2 g (91%) of N-deuterio-α-nitrobenzylidene phenylhydrazine: mp 103–104 °C; NMR ($CDCl_3$) δ 7.0–7.8 (m, ring H) and 12.1 (s, 0.1, NH); mass spectrum (75 eV) m/e (rel intensity) 244 (1.66), 243 (15.3), 242 (100.0), and 241 (20.5).

Benzamidrazone Hydrochloride. A 75-ml absolute ethanol solution containing 1.0 g (0.004 mol) of 2 (R = C_6H_5) and 0.1 g of 60% palladium chloride was treated with hydrogen under a pressure of 40 psi for 3 h. Filtration and concentration of the solution in vacuo gave an oil. It was dissolved in anhydrous ether and treated with hydrogen chloride at 10 °C. A white precipitate formed which was filtered and dried in vacuo to give 1.0 g (98%) of benzamidrazone hydrochloride: mp 123–125 °C dec (lit.[19] mp 124 °C dec); ir (KBr) 3400–2500 ($-NH_3^+$) and 1605 cm^{-1} (C=N).

3-Nitrobenzylidene Methylphenylhydrazine (12). The general procedure was used as described in experiment B except that 8.4 g (0.075 mol) of potassium tert-butoxide, 18.1 g (0.075 mol) of 3-nitrobenzylidene phenylhydrazine (11), and 15.75 g (0.15 mol) of n-propyl nitrate were employed in 250 ml of THF. No apparent reaction occurred upon the addition of n-propyl nitrate as judged by the lack in color change of the reaction mixture. After 30 min, the reaction mixture was cooled to −40 °C and 21.4 g (0.15 mol) of methyl iodide added dropwise. After 30 min, the solution was warmed to −10 °C and 9.0 g 0.15 mol) of glacial acetic acid added. The green suspension was filtered at room temperature and the filtrate concentrated in vacuo to afford 13.0 g (100%) of 3-nitrobenzylidene methylphenylhydrazine (95% C_2H_5OH): mp 111–112 °C (lit.[18] mp 112 °C); NMR ($CDCl_3$) δ 3.36 (s, 3, NCH_3) and 6.8–8.1 (m, 10, ring H and CH).

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Registry No.—1 (R = C_6H_5), 588-64-7; 1 (R = 2-$MeOC_6H_4$), 21968-29-6; 1 (R = 4-$MeOC_6H_4$), 622-73-1; 1 (R = 2-MeC_6H_4), 59473-50-6; 1 (R = 4-MeC_6H_4), 2829-25-6; 1 (R = 2-ClC_6H_4), 34158-76-4; 1 (R = 4-ClC_6H_4), 2829-26-7; 1 (R = 4-BrC_6H_4), 16917-42-3; 1 (R = 4-$Me_2CHC_6H_4$), 10407-16-6; 1 (R = 4-$CF_3C_6H_4$), 59473-51-7; 1 (R = 1-naphthyl), 24090-98-0; 1 (R = 2-naphthyl), 24091-13-2; 1 (R = 2-furyl), 2216-75-3; 1 (R = 2-thienyl), 39677-96-8; 1 (R = 3-pyridyl), 57023-37-7; 1 (R = H), 6228-40-6; 1 (R = Me), 935-07-9; 1 (R = Pr), 940-54-5; E-2 (R = C_6H_5), 59473-52-8; Z-2 (R = C_6H_5), 55849-26-8; E-2 (R = 2-$MeOC_6H_4$), 59473-53-9; Z-2 (R = 2-$MeOC_6H_4$), 59473-54-0; E-2 (R = 4-$MeOC_6H_4$), 59473-55-1; Z-2 (R = 4-$MeOC_6H_4$), 59473-56-2; E-2 (R = 2-MeC_6H_4), 59473-57-3; Z-2 (R = 2-MeC_6H_4), 59473-58-4; E-2 (R = 4-MeC_6H_4), 59473-59-5; Z-2 (R = 4-MeC_6H_4), 59473-60-8; E-2 (R = 2-ClC_6H_4), 59473-61-9; Z-2 (R = 2-ClC_6H_4), 59473-62-0; E-2 (R = 4-ClC_6H_4), 59473-63-1; Z-2 (R = 4-ClC_6H_4), 59473-64-2; E-2 (R = 4-BrC_6H_4), 59473-65-3; Z-2 (R = 4-BrC_6H_4), 59473-66-4; E-2 (R = 4-$Me_2CHC_6H_4$), 59473-67-5; Z-2 (R = 4-$Me_2CHC_6H_4$), 59473-68-6; E-2 (R = 4-$CF_3C_6H_4$), 59473-69-7; Z-2 (R = 4-$CF_3C_6H_4$), 59473-70-0; E-2 (R = 1-naphthyl), 59473-71-1; Z-2 (R = 1-naphthyl, 59473-72-2; E-2 (R = 2-naphthyl), 59473-73-3; Z-2 (R = 2-naphthyl), 59473-74-4; E-2 (R = 2-furyl), 59473-75-5; Z-2 (R = 2-furyl), 59473-76-6; E-2 (R = 2-thienyl), 59473-77-7; Z-2 (R = 2-thienyl), 59473-78-8; E-2 (R = 3-pyridyl), 59473-79-9; Z-2 (R = 3-pyridyl), 59473-80-2; E-2 (R = H), 59473-81-3; Z-2 (R = H), 59473-82-4; E-2 (R = Me), 55849-27-9; Z-2 (R = Me), 55849-23-5; E-2 (R = Pr), 55849-29-1; Z-2 (R = Pr), 55849-25-7; 3, 17355-78-1; 4, 59473-83-5; 7, 59473-84-6; 8, 59473-85-7; 9, 59473-86-8; 10, 59473-87-9; 11, 7539-23-3; 12, 23718-95-8; benzamidrazone HCl, 39696-43-0.

Supplementary Material Available. Full analytical and spectroscopic data (ir, uv, NMR, mass spectra) for compounds 2 listed in Table II are presented (6 pages). Ordering information is given on any current masthead page.

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