spectral properties with authentic samples.

Several solvents, bases, and stoichiometries for **1a** and **1b** were carried out with benzylamine and dibenzylamine by using the same general procedure. After the most suitable conditions were established, various primary and secondary amines were oxidized as described above and the results are collected in Table II. Precautions worthy of note are that, (a) the amines and reaction mixtures must be protected from carbon dioxide in the atmosphere to prevent carbamate salt formation and reduced yields and (b) rotary evaporation and then hydrolysis must be carried out as quickly as possible (without heating) to minimize condensation of the imine product.

In most cases the residue from the steam distillation was basified with potassium hydroxide, extracted with methylene chloride (3 × 10 mL), and analyzed for the starting amine by gas chromatography. Only small (3-5%) amounts of the amines were detected.

Reactions of Imines 4a-d with 1b. A solution of the imine (1.5 mmol) in ethyl acetate was treated with **1b** (1.5 mmol), and the mixture was allowed to stand at room temperature. The active oxygen was monitored by iodometric titration. Loss of peroxide usually took longer than 20 h, and the products (after hydrolysis) were the carbonyl and amine components of the starting imine (85-100%) and products from the decomposition of **1b**, mostly *m*-(trifluoromethyl)benzenesulfonic acid (80-90%).

Reaction of 5 with 1b. Methyleneaniline trimer, **5**, (1.5 mmol) was dissolved in ethyl acetate (30 mL), cooled to -78 °C, and treated with **1b** (1.5 mmol). Loss of active oxygen was complete after several minutes and no volatile products were obtained after the usual workup.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation to whom we are deeply grateful.

Registry No. **1a**, 6209-72-9; **1b**, 35673-10-0; **2**, 100-46-9; **3**, 103-49-1; **4a**, 6700-95-4; **4b**, 32838-32-7; **4c**, 780-25-6; **4d**, 41882-47-7; **5**, 91-78-1; $CH_3(CH_2)_5NH_2$, 111-26-2; $CH_3(CH_2)_7NH_2$, 111-86-4; $CH_3(CH_2)_5CH(NH_2)CH_3$, 693-16-3; $PhCH(CH_3)NH_2$, 98-84-0; $[CH_3(CH_2)_5]_2NH$, 143-16-8; $[CH_3(CH_2)_7]_2NH$, 1120-48-5; $PhCH_2NHCH_3$, 103-67-3; PhCHO, 100-52-7; $CH_3(CH_2)_4CHO$, 66-25-1; $CH_3(CH_2)_6CHO$, 124-13-0; $CH_3(CH_2)_5C(O)CH_3$, 111-13-7; $PhC(O)CH_3$, 98-86-2; cyclohexylamine, 108-91-8; dicyclohexylamine, 101-83-7; cyclopentylamine, 1003-03-8; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3.

Oxidation of Hydrazine Derivatives with Arylsulfonyl Peroxides[1]

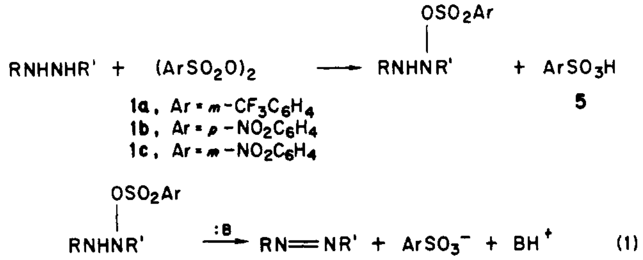
Robert V. Hoffman* and Anil Kumar

Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003

Received February 14, 1984

A new method for the generation of the azo function is reported. A series of hydrazine derivatives, which included alkyl- and arylhydrazines, monoacylhydrazides, and diacylhydrazides, was oxidized with *m*-(trifluoromethyl)benzenesulfonyl peroxide. Smooth conversion to the diimide was observed. The diimides then yielded products typical of normal degradation pathways.

Amines react nucleophilically with arylsulfonyl peroxides to give *N*-arylsulfonoxy derivatives which undergo facile elimination to imines.[2] It would be useful to extend this chemistry to the oxidation of hydrazine derivatives with arylsulfonyl peroxides. If an analogous two-step reaction pathway were followed for hydrazines, (eq 1), then a new method for generating the azo linkage would be realized.



$$\mathrm{RNHNHR'} + (\mathrm{ArSO_2O})_2 \longrightarrow \mathrm{RNHN(OSO_2Ar)R'} + \underset{\mathbf{5}}{\mathrm{ArSO_3H}}$$

1a, Ar = *m*-$CF_3C_6H_4$
1b, Ar = *p*-$NO_2C_6H_4$
1c, Ar = *m*-$NO_2C_6H_4$

$$\mathrm{RNHN(OSO_2Ar)R'} \xrightarrow{:B} \mathrm{RN{=}NR'} + \mathrm{ArSO_3^-} + \mathrm{BH^+} \qquad (1)$$

A good number of preparative routes to azo compounds are available.[3] The most widely applicable route, however, is the oxidation of hydrazine derivatives.[4] A variety of oxidants can be used, but many of these reagents exhibit a lack of generality, structure sensitivity, overoxidation, or side reactions. Therefore there is a continuing search for new oxidants which may circumvent some of these problems.

Table I. Oxidation of Monosubstituted Hydrazines 2 with mTFBSP[a]

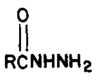
hydrazine	product (% yield)[b]
$C_6H_5NHNH_2$, **2a**	C_6H_6 (73) $C_6H_5N{=}NC_6H_5$ (4.7)
p-$CH_3C_6H_4NHNH_2$, **2b**	$CH_3C_6H_5$ (63)
p-$ClC_6H_4NHNH_2$, **2c**	ClC_6H_5 (47)
$C_6H_5CH_2NHNH_2$, **2d**	$C_6H_5CH_3$ (51) C_6H_5CHO (25)

[a] Reactions were carried out in dichloromethane at -78 °C. [b] Yields based on the peroxide oxidant averaged from two or more experiments.

Based on the good nucleophilicity of hydrazines and the mild conditions under which elimination in *N*-arylsulfonoxy compounds takes place, it was felt that sulfonyl peroxides might be excellent general oxidants for hydrazines. Several hydrazine derivatives, **2-4**, were chosen for study and the results are reported herein.

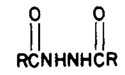
$RNHNH_2$

2



$RC(=O)NHNH_2$

3



$RC(=O)NHNHC(=O)R$

4

Results and Discussion

Monosubstituted Hydrazines 2. Slow addition of a dichloromethane solution of *m*-(trifluoromethyl)benzenesulfonyl peroxide, **1a**, mTFBSP, to a solution of the hydrazine **2a-d** at -78 °C followed by exposure to air gave

---

[1] Taken in part from the Ph.D Thesis of A.K. submitted to the Graduate School of New Mexico State University, October, 1983.

[2] (a) Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2183. (b) Hoffman, R. V.; Belfoure, E. L. *Ibid.* **1979**, *101*, 5687. (c) Hoffman, R. V.; Cadena, R. *Ibid.* **1977**, *99*, 8226.

[3] Sandler, S. R.; Karo, W. "Organic Functional Group Preparations"; Academic Press: New York, 1971, Vol. 2.

[4] Newbold, B. T. In "The Chemistry of the Hydrazo, Azo, and Azoxy Groups"; Patai, S., Ed.; Wiley: London, 1971; Part 1, Chapter 14, p 541.

0022-3263/84/1949-4014$01.50/0

the corresponding hydrocarbon in good yields (Table I). While several arylsulfonyl peroxides **1a–c** gave similar results, mTFBSP was used exclusively due to its good solubility characteristics. As seen in eq 1, 2 equiv of *m*-(trifluoromethyl)benzenesulfonic acid, **5**, are produced in the oxidation so an excess of the hydrazine is required.

Several observations implicate a diimide as the primary oxidation product. Firstly, it was necessary to expose the reaction mixture to the atmosphere (O_2) prior to workup to get satisfactory yields. Kosower[5] and others[6] have shown that monosubstituted diimides undergo rapid reaction with oxygen to give the hydrocarbon product (eq 2). In the

$$RN{=}NH \xrightarrow[\text{fast}]{O_2} RH + N_2 \qquad (2)$$

absence of oxygen, other reactions occur. Since the yield of hydrocarbon in these oxidations is found to depend on exposure of the reaction mixture to air, it is likely that the diimide is also the hydrocarbon precursor.

Secondly, the corresponding arylazo compound was always detected in the product mixture by thin-layer chromatography (TLC), and azobenzene (4.7%) was isolated from the oxidation of **2a**. It is also known that aryldiazenes undergo a bimolecular reaction which gives the hydrocarbon and hydrazo compound (eq 3).[7] The

$$2RN{=}NH \rightarrow RH + {}^1/{}_2RNHNHR + N_2 \qquad (3)$$

hydrazobenzene could be air-oxidized to azobenzene or, more likely, oxidized by the sulfonyl peroxide, since we have found that hydrazobenzene is also oxidized efficiently to azobenzene (70%) by mTFBSP.

Thirdly, if phenylhydrazine (**2a**) is oxidized with 2 equiv of **1a**, the phenyldiazonium ion is produced (eq 4) as evidenced by formation of its β-naphthol diazonium coupling product (23%) and its conversion to chlorobenzene by cuprous chloride (25%). Further oxidation of the diazene intermediate by mTFBSP is the most probable origin of the diazonium ion.

$$4PhNHNH_2 + 2(ArSO_2O)_2 \rightarrow PhN_2^+\ ArSO_3^- + 3PhNHNH_3ArSO_3^- \qquad (4)$$

The above results firmly implicate diimides as the products of oxidation of hydrazines **2** by mTFBSP, and they are quite similar to the oxidation of **2a** by lead tetraacetate (LTA). Aylward reported that **2a** gave phenyldiimide and then benzenediazonium acetate upon LTA oxidation.[8] Back has noted an analogous two-stage oxidation of arylhydrazines with benzeneseleninic acid and anhydride.[9]

The mechanism by which diimides are produced by **1a** is less certain. The oxidation of benzylhydrazine, **2d**, gives toluene (51%) and benzaldehyde (25%). While toluene is the product expected from the decomposition of the intermediate diimide **6**, benzaldehyde most likely arises from the hydrolysis of benzaldehyde hydrazone **7**. Hydrazone **7** could be produced via several plausible routes. Analogous to the oxidation of amines by sulfonyl peroxides,[2] **2d** and **1a** could give *N*-sulfonoxy derivatives **8** and **9** (Scheme I). While a variety of factors influence the regiochemistry of the attachment of electrophiles to hydrazines,[10] adduct **8** would normally be favored due to the higher nucleophilicity of the internal nitrogen. Elimination in **8** could occur to give both **6** and **7** and hence the observed products. Due to the higher acidity of the N–H bond, diimide **6** would be favored kinetically. However, thermodynamic factors have been shown to have an important influence in the regiochemistry of elimination in *N*-sulfonoxy derivatives,[2c] thus the more stable[11] **7** would be thermodynamically favored. These competing factors might account for the observed mixture.

Scheme I

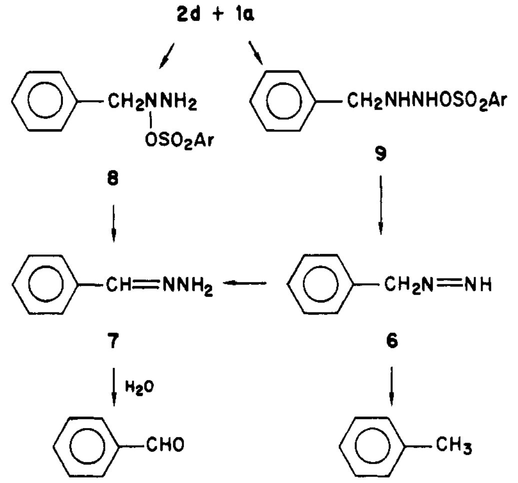


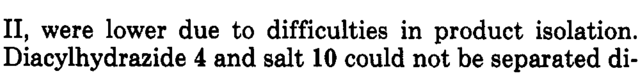
Table II. Oxidation of Monoacylhydrazines 3 with mTFBSP[a]

acylhydrazine $RCONHNH_2$, R =	product	yield,[b] %
C_6H_5, **3a**	$(C_6H_5CONH)_2$, **4a**	68
m-ClC_6H_4, **3b**	(*m*-$ClC_6H_4CONH)_2$, **4b**	58
p-$CH_3OC_6H_4$, **3c**	(*p*-$CH_3OC_6H_4CONH)_2$, **4c**	40
m-$CH_3C_6H_4$, **3d**	(*m*-$CH_3C_6H_4CONH)_2$, **4d**	50
c-C_6H_{11}, **3e**	(c-$C_6H_{11}CONH)_2$, **4e**	32

[a] Reactions were carried out in dichloromethane at 25 °C. [b] Isolated pure product based on the peroxide oxidant averaged from two or more experiment.

Another possibility for the origin of **7** is that diimide **6** tautomerizes to **7**. Such tautomerizations are well-known in azoalkanes, but since strong acids or bases or free radical initiators are normally required,[12] this pathway is less likely in the present study. Based on amine precedents,[2] we prefer the two-step pathway of Scheme I over electron-transfer routes, but our data do not exclude the latter possibilities.

Monoacylhydrazines. Acid hydrazides **3** are much less reactive toward **1a** than arylhydrazines **2**. Nevertheless, increasing the reaction temperature to 25 °C gave smooth oxidation of **3** to the corresponding diacylhydrazines **4** in high yields as determined by infrared spectroscopy of the crude products (eq 5). Isolated yields, reported in Table II, were lower due to difficulties in product isolation. Diacylhydrazide **4** and salt **10** could not be separated directly as both had very similar, low solubilities. Treatment of the product mixture with base gave a mixture of the mono- and bishydrazides **3** and **4** which could be partially separated by flash chromatography.[13] The yields in Table II are given for pure, isolated **4**; additional material con-



$$4R\overset{\overset{O}{\|}}{C}NHNH_2 + \mathbf{1a} \longrightarrow R\overset{\overset{O}{\|}}{C}NHNH\overset{\overset{O}{\|}}{C}R + N_2 + 2R\overset{\overset{O}{\|}}{C}NHN^+H_3\ ArSO_3^- \qquad (5)$$

3 4 10

---

[5] Huang, P. C.; Kosower, E. M. *J. Am. Chem. Soc.* **1967**, *89*, 3910, 3911.

[6] Nicholson, J.; Cohen, S. G. *J. Am. Chem. Soc.* **1966**, *88*, 2247.

[7] Huang, P. C.; Kosower, E. M. *J. Am. Chem. Soc.* **1968**, *90*, 2367.

[8] Aylward, J. B., *J. Chem. Soc. C* **1969**, 1663.

[9] Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1981**, *46*, 1564.

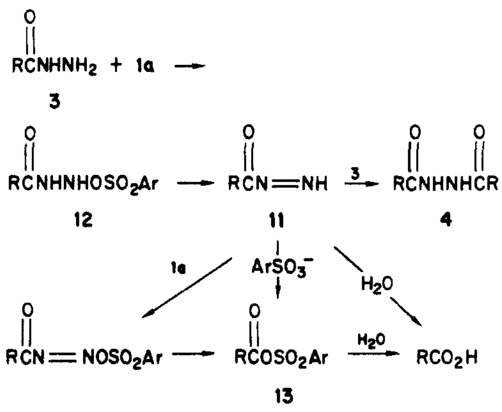
[10] Hegarty, A. F. in ref 4, Part 2, Chapter 16, p 643.

[11] Bellamy, A. J.; Guthrie, R. D.; Chittenden, G. J. F. *J. Chem. Soc. C* **1966**, 1989.

[12] Bellamy, A. J.; Guthrie, R. D. *J. Chem. Soc.* **1965**, 3528, 2778.

[13] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Scheme II



taminated with varying amounts of **3** was not included. A second product detected in all cases by TLC, but isolated only for **3a** (12%), was the corresponding carboxylic acid.

The production of diacylhydrazides **4** from **3** likely occurs via acyldiimide **11**. These species are known to be good acylating agents and react with excess **3** to give the bis product (Scheme II). The diacylhydrazide **4** is also a major product from the oxidation of **3** with both selenium oxidants,[9] lead tetraacetate,[14] and halogens,[23] which are also thought to first give the acyldiimide **11**. The carboxylic acid could have a variety of origins, all of which stem from the diimide **11**. Since reasonable care was taken to exclude moisture, direct reaction of **11** with water is the least likely source. Further oxidation of **11** or its reaction with arenesulfonate ions present in solution could both lead to the mixed anhydride **13** which would give the acid by hydrolysis. Our working hypothesis is that the more nucleophilic terminal nitrogen[10] of **3** gives the N-sulfonoxy adduct **12** which eliminates to diimide **11**. While other oxidation mechanisms cannot be excluded, the above hypothesis is simple, direct, and based on analogy to amine oxidations with sulfonyl peroxides.[2]

1,2-Diacylhydrazines. Dibenzoylhydrazide, **4a**, reacted smoothly at room temperature with **1a** in dichloromethane to give an orange solution which showed the presence of the diacyl diimide by TLC. However, the color faded with time and no simple products could be isolated from the reaction mixture. A control experiment showed that the sulfonic acid produced in the oxidation caused decomposition of the diimide product. Diaroyldiimides are known to react with alcohols to give esters.[15,16] Oxidations of **4** were therefore carried out in a mixture of dichloromethane and alcohols. Again a red or pink coloration and TLC analysis indicated that the diimide was produced, but esters were isolated in good yields according to eq 6. The

$$\mathrm{RCONHNHCOR} + \mathbf{1a} \xrightarrow{\mathrm{R'OH}} \mathrm{2RCO_2R'} \qquad (6)$$

results are presented in Table III. Some starting hydrazide **4** was always recovered (15–20%). Control reactions showed that **4a** itself did not yield ester under the reaction conditions. Furthermore, in the presence of *m*-(trifluoromethyl)benzenesulfonic acid, authentic diimide **14a** reacted with ethanol to give ethyl benzoate (60%) and dibenzoylhydrazine, **4a** (10%), eq 7.

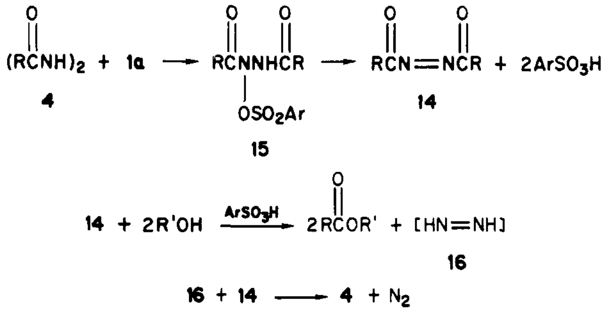
$$\mathrm{C_6H_5CON{=}NCOC_6H_5} \xrightarrow[\mathrm{ArSO_3H}]{\mathrm{EtOH}} \mathrm{C_6H_5CO_2Et} + \mathrm{(C_6H_5CONH)_2} \qquad (7)$$

Table III. Oxidation of 1,2-Diacylhydrazides 4 with mTFBSP in the Presence of Alcohols[a]

hydrazine (RCONH)$_2$, R =	product	yield,[b] %
C_6H_5, **4a**	$C_6H_5CO_2Et$	86
m-ClC_6H_4, **4b**	*m*-$ClC_6H_4CO_2Me$	54
p-$CH_3C_6H_4$, **4c**	*p*-$CH_3OC_6H_4CO_2Me$	62
m-$CH_3C_6H_4$, **4d**	*m*-$CH_3C_6H_4CO_2Me$	81
c-C_6H_{11}, **4e**	c-$C_6H_{11}CO_2Me$	78

[a] Ethanol used for **4a**, methanol used for **4b–e**. [b] Yields determined by gas chromatography averaged for two or more runs.

Scheme III



These observations are consistent with the reaction scenario shown in Scheme III. The oxidation of 1,2-diacylhydrazines **4** to the diimide **14** occurs smoothly. The diimide is a good acylating agent and reacts with added alcohols to give the ester product and diimide, **16**, which can reduce some of **14** back to the starting hydrazide **4**. This is fully consistent with the control reaction where authentic **14** also returns **4** under the reaction conditions.

Literature precedents are consistent with Scheme III since α-carbonylazo compounds are known to be effective acylating agents which react rapidly with alcohols to give esters.[16] Furthermore, the reaction of **14** with methoxide also gives methyl benzoate and diacylhydrazide **4**, substantiating the propensity of diimide **16** to effectively reduce the azo function of **14**.[17] Analogous behavior is seen in azodicarboxylates.[18]

Based on the spectrum of results presented above, it is clear that **1a** (and arylsulfonyl peroxides in general) effectively oxidizes hydrazo precursors to azo products. While we have presented only a survey of the reaction processes, the results are consistent with a mechanism analogous to amine oxidations that involves the formation and elimination of an *N*-sulfonoxy intermediate.

While this method represents a new method to generate the —N=N— function, the products ultimately obtained are similar to those found in other oxidations. The products reflect reactivity of the azo function rather than influence of the oxidant. A fundamental problem in the use of sulfonyl peroxides is that 2 equiv of the sulfonic acid are formed in the oxidation. If the hydrazine is basic (e.g., **2**, **3**) an excess of the hydrazine is needed to scavenge this acid, or where the hydrazine is not so basic (e.g., **4**) the acid catalyzes decomposition of the products. If this problem could be circumvented, then sulfonyl peroxides could be very useful reagents for hydrazine oxidation. Such will be the goals of future work in this area.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as liquid films (liquids) or potassium bromide disk (solids); NMR spectra were taken on a

---

(14) Gladstone, W. A. F. *J. Chem. Soc. C* **1969**, 1571.

(15) Leffler, J. E.; Bond, W. B. *J. Am. Chem. Soc.* **1957**, *78*, 335.

(16) Cohen, S. G.; Nicholson, J. *J. Org. Chem.* **1965**, *30*, 1162.

(17) Bumgardner, C. L.; Purrington, S. T.; Huang, P. *J. Org. Chem.* **1983**, *48*, 2287.

(18) White, R. E.; Kovacic, P. *J. Am. Chem. Soc.* **1974**, *96*, 7284.

JEOL PS-100 instrument; and mass spectra were taken on a Hitachi RMU-6 mass spectrometer. Gas chromatography was performed on either a Varian A-90-P-3 or a Varian 920 gas chromatograph. Volatile products were analyzed on a column of QF-1 (6.2 mm × 2.5 m, 5%, Anachrome 80/90-mesh support). Detector response factors were calculated from known mixture and applied to the raw peak area data.

Sulfonyl peroxide **1a** was prepared by literature methods.[19] Hydrazines **2** were prepared by the reaction of hydrazine with methyl esters of the corresponding carboxylic acids.[21] Diacylhydrazines **4** were prepared by the reaction of hydrazine with the corresponding acid chlorides.[22] Dibenzoyldiimide, **14**, was prepared by a literature method.[23] Solvents were reagent grade and distilled before use.

Oxidation of Monosubstituted Hydrazines 2 with 1a. All oxidations were carried out similarly as follows: A solution of the hydrazine (4 mmol) in dichloromethane (35 mL) under nitrogen was cooled to −78 °C. A cooled (−78 °C) solution of mTFBSP (1 mmol) in dichloromethane (15 mL) was added over 15 min, and the reaction mixture was stirred at −78 °C for 5 h after which it was uncapped and allowed to come to room temperature with stirring (2 h). The reaction mixture was filtered, and the filtrate was extracted with water (1 × 25 mL), dried ($MgSO_4$), and analyzed by gas chromatography for the hydrocarbon product after addition of a suitable standard. Yields are given in Table I.

Detection of Benzene Diazonium Ion in the Oxidation of 2a with Excess 1a. a. β-Naphthol Derivative. Phenylhydrazine (432 mg, 4 mmol) was oxidized with **1a** (900 mg, 2 mmol) as described above; however, the reaction mixture was filtered cold and the solid obtained was suspended in dichloromethane (5 mL) at 0 °C. A cooled (0 °C) solution of β-naphthol (310 mg, 2.1 mmol) and potassium hydroxide (400 mg) in water was added, and the mixture was stirred 30 min at 0 °C to give a thick red-orange mixture. After being diluted with water (15 mL), the reaction mixture was extracted with ether (3 × 10 mL), and the ether extracts were dried ($MgSO_4$). Solvent removal and chromatography on silica gel delivered 1-(phenylazo)-2-hydroxynaphthalene (23%), mp 130–131 °C (lit.[24] mp 133–134 °C). The IR and NMR spectra and the R_f value upon TLC matched those of an authentic sample.

b. Sandmeyer Reaction. Phenylhydrazine (4 mmol) was oxidized with **1a** (2 mmol) as described above. To the cold reaction mixture was added a cooled (5 °C) solution of cuprous chloride (70 mg, 0.8 mmol) in concentrated hydrochloric acid (0.5 mL). The biphasic mixture was stirred vigorously at −78 °C (10 min) and then heated to 60 °C (15 min). The resulting mixture was filtered, and the filtrate was washed successively with water, 10% sodium hydroxide, and water. The solution was dried ($MgSO_4$) and analyzed by gas chromatography for chlorobenzene (25%).

Oxidation of Hydrazobenzene with 1a. To hydrazobenzene (276 mg, 1.5 mmol) in cold (−78 °C) dichloromethane (30 mL) was added **1a** (225 mg, 0.5 mmol), and the mixture was stirred for 30 min at −78 °C. The cold reaction was filtered, the solvent removed by rotary evaporation, and the residue chromatographed on silica gel (hexane:chloroform, 1:1). The azobenzene was the first component eluted (70%) and was identical with an authentic sample.

Oxidation of Monoacylhydrazides 3 with 1a. The same general procedure was followed: To the hydrazide **3** (4 mmol) in dichloromethane (40 mL) under nitrogen was added **1a** (1 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature for 3 h after which it was filtered. The solid product was stirred with 10% sodium hydroxide (20 min), filtered, washed with water, and air-dried. Flash chromatography of the product[13] gave the bishydrazide **4** as the first band; however, later fractions of this band were contaminated with **3** and were discarded. The diacylhydrazides **4** were identified by comparison of melting points and IR spectra with authentic samples. Yields are reported in Table II.

In the oxidation of benzoylhydrazine **4a** the filtrate of the reaction mixture was washed with saturated sodium bicarbonate (2 × 15 mL). The aqueous layer was acidified with 2.5 N hydrochloric acid and extracted with ether (3 × 10 mL), and the ether extracts were dried ($MgSO_4$) and evaporated to give benzoic acid (12%) which was identified by its melting point and IR spectrum.

Oxidation of 1,2-Diacylhydrazines 4 with 1a. To a cooled (0 °C) suspension of the bishydrazide **4** (1 mmol) in a 1:1 mixture of dichloromethane and alcohol (40 mL) was added **1a**, and the orange mixture was stirred at 0 °C until the orange color disappeared (1–3 h). The reaction was stirred at room temperature overnight, and the resulting clear solution was extracted with water (2 × 15 mL), dried ($MgSO_4$), and analyzed for the ester by gas chromatography after addition of a suitable standard. Yields are given in Table III.

Reaction of 4a with Ethanol. A suspension of **4a** (240 mg, 1 mmol) and *m*-(trifluoromethyl)benzenesulfonic acid (30 mg) in a 1:1 dichlormethane:ethanol (40 mL) was stirred overnight at room temperature. The mixture was filtered, extracted with water (2 × 15 mL), dried ($MgSO_4$), and analyzed by gas chromatography. No ethyl benzoate was detected. The filtered solid (210 mg) was found to be **4a**.

Reaction of Dibenzoyldiimide, 14a, with Ethanol. *m*-(Trifluoromethyl)benzenesulfonic acid (30 mg) was added to a solution of **14a** (100 mg, 0.4 mmol) in 1:1 dichloromethane:ethanol (40 mL), and the mixture was stirred overnight. The reaction mixture was filtered and the solid was identified as dibenzoylhydrazine **4a** (10 mg, 10%) by its IR spectrum. The filtrate was worked up as above and found to contain ethyl benzoate (60%) by gas chromatography.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the National Science Foundation to whom we are grateful.

Registry No. **1a**, 35673-10-0; **2a**, 100-63-0; **2b**, 539-44-6; **2c**, 1073-69-4; **2d**, 555-96-4; **3a**, 613-94-5; **3b**, 1673-47-8; **3c**, 3290-99-1; **3d**, 13050-47-0; **3e**, 38941-47-8; **4a**, 787-84-8; **4b**, 38192-14-2; **4c**, 849-82-1; **4d**, 1530-73-0; **4e**, 5814-04-0; PhNHNHPh, 122-66-7.

---

[19] Dannley, R. L.; Tornstrom, P. K. *J. Org. Chem.* **1975**, *40*, 2278.

[20] Purchased from Aldrich Chemical Co.

[21] Smith, P. A. S. *Org. React. (N.Y.)* **1946**, *3*, Chapter 9.

[22] Hyatt, H. H. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. 2, p 208.

[23] Imamoto, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2216.

[24] Weast, R. C., Selby, S. M., Eds. "Handbook of Chemistry and Physics"; Chemical Rubber Co.: Cleveland, OH, 1966.