Reaction of *N*-Nitrosodibenzylamine with Phenacyl Bromides

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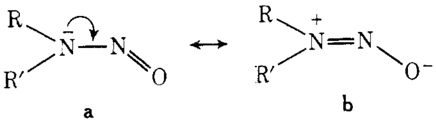
The reaction of *N*-nitrosodibenzylamine (NDBA) with phenacyl bromides in the presence of silver hexafluoroantimonate proceeds via the intermediacy of *N*-dibenzylaminonitrene in ether to give bibenzyl and benzylidenedibenzylhydrazine. In benzene as solvent, diphenylmethane is the major product. In all cases, benzaldehyde was formed, sometimes as the major product of the reaction. Possible mechanisms for these transformations are discussed.

For some time we have been interested in novel methods to generate *N*-nitrenes (1). In principle, *N*-nitrosamines (2) could serve as precursors of *N*-nitrenes if they are regarded as *N*-nitrene *N*-oxides, a view supported by the large contribution of mesomeric form **2b** to the structure of *N*-nitrosamines.[1] These considerations coupled with the current interest in the chemistry[2] and biological activity of *N*-nitrosamines[3] prompted the investigation herein described.



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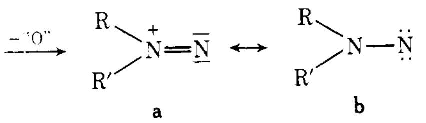

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The "deoxygenation" of *N*-nitrosamines has been previously accomplished with ethyl diphenylphosphinite,[4] iron pentacarbonyl,[5] and aryl azides.[6] The oxidation of α-halo carbonyl compounds by compounds such as sulfoxides and amine *N*-oxides[7] suggested that *N*-nitrosamines could similarly be "deoxygenated" to *N*-nitrenes. Indeed it was anticipated that phenacyloxy diazenium ions 7 if formed would surrender a proton to an external base to yield the *N*-nitrenes and the α-dicarbonyl compounds.

Results and Discussion

For reasons discussed earlier,[6] *N*-nitrosodibenzylamine (NDBA, **2**, R = R′ = PhCH$_2$) was chosen as the substrate for our investigation. Since *N*-nitrosamines had been reported to be *O*-alkylated by powerful alkylating agents such as trialkyloxonium salts,[8] the reactions of NDBA were carried out with phenacyl bromides **3** and silver hexafluoroantimonate (actually compex **9** is believed to be the reactive species as shown in eq 4).[9]

$$\underset{\mathbf{3}}{ArCOCH_2Br} + AgSbF_6 \rightarrow \underset{\mathbf{4}}{[ArCOCH_2^+SbF_6^-]} + AgBr \qquad (1)$$

a, Ar = C_6H_5; **b**, Ar = p-BrC_6H_4; **c**, Ar = p-$NO_2C_6H_4$

The reactions of NDBA with **4** are summarized in Table I. In diethyl ether as solvent (Table I, experiments 7, 11, and 13), bibenzyl (**5**) and benzylidenedibenzylhydrazine (**6**) were isolated and characterized. Their formation can be understood in terms of further reactions of *N*-dibenzylaminonitrene (**1**, R = R′ = PhCH$_2$) as shown in Scheme I.[10]

$$\mathbf{1} \rightarrow \underset{\mathbf{5}}{PhCH_2CH_2Ph} + \underset{\mathbf{6}}{PhCH{=}NN(CH_2Ph)_2} \qquad (2)$$

In most cases, benzaldehyde was a major product of the reaction. Its formation may be rationalized via removal of one of the benzylic hydrogens of **7** as shown in Scheme II.[11]

The results of the reaction of phenacyl bromide with silver hexafluoroantimonate followed by addition of NDBA in wet ether (experiment 7) were informative. The appearance of

Table I. Reaction of ArCOCH$_2$Br (3) with NDBA in the Presence of AgSbF$_6$[a]

	ArCOCH$_2$Br (3) (mmol)	Registry No.	NDBA,[b] mmol	AgSbF$_6$, mmol	Et$_3$N, mL	Solvent[c] (mL)	Products, %[a]				
							5	6	10	PhCHO	Others
1	C_6H_5 (7)	70-11-1		7		B (20)					*d*
2			7	7	10	B (20)					*e*
3	C_6H_5 (4)		4			B (10)					*f*
4	C_6H_5 (10)		10	10	10	B (25)	4		42	Traces	*g*
5	C_6H_5 (10)		10	10		B (25)	4		37	19	*h*
6	C_6H_5 (10)[i]		10	10	10	B (25)	5		15		*i*
7	C_6H_5 (10)		10	10	10	E (25)	13	10		10	*j*
8	C_6H_5 (10)		10	10		E (25)	4	4		21	*k*
9	p-BrC_6H_4 (8.4)	99-73-0	8.4	8.4	8.4	B (20)	10		45	Traces	*l*
10	p-BrC_6H_4 (10)		10	10		B (25)	6		43	16	*m*
11	p-BrC_6H_4 (10)		10	10	10	E (25)	11	12		23	*n*
12	p-$NO_2C_6H_4$ (10)	99-81-0	10	10	10	B (25)	11		40	Traces	*o*
13	p-$NO_2C_6H_4$ (10)		10	10	10	E (20)	10	18		15	*p*

[a] Reactions were carried out at reflux for 24 h; in experiments where Et$_3$N was used, the reaction mixture was heated for an additional 24 h after the addition. Yields are based on starting material used and were divided by 2 for **10** and multiplied by 2 for **6**. [b] NDBA = *N*-nitrosodibenzylamine (**2**, R = R′ = PhCH$_2$). [c] B = benzene; E = diethyl ether. [d] Phenacyl bromide, 96%. [e] NDBA, 96%. [f] Phenacyl bromide, 95%; and NDBA, 95%. [g] Benzil, 21%. [h] Benzil, traces; benzoic acid, 12%; and phenacyl bromide, 6%. [i] Reaction of phenacyl bromide and AgSbF$_6$ was heated at reflux for only 3 h. [j] NDBA, 10%. [k] Phenacyl alcohol, 94%; NDBA, 23%; and phenacyl bromide 5%. [l] p-Bromobenzil, 13%; and NDBA, traces. [m] p-Bromobenzoic acid, 5%; p-bromophenacyl bromide, 4%; and p-Bromobenzil, 12%. [n] NDBA, 24%. [o] p-Nitrobenzil, 8.4%. [p] NDBA, 11%.

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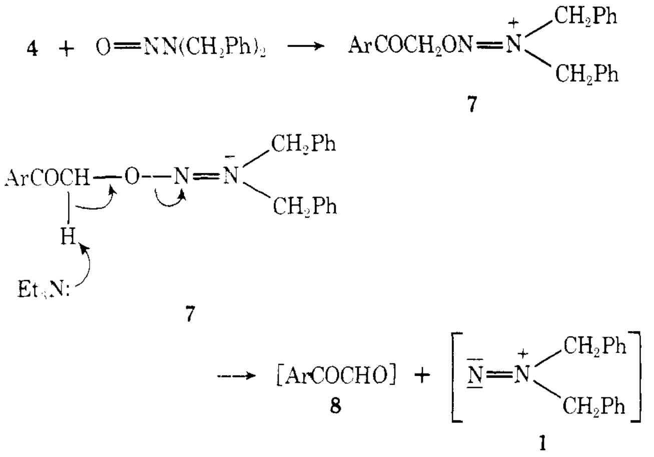
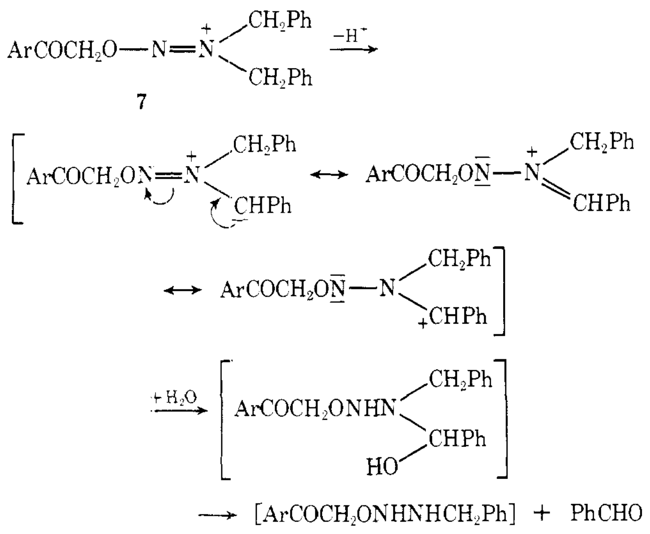
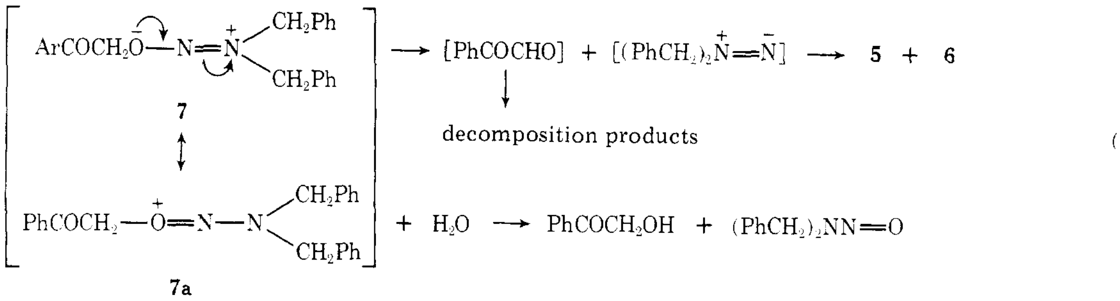
Scheme I



Scheme II

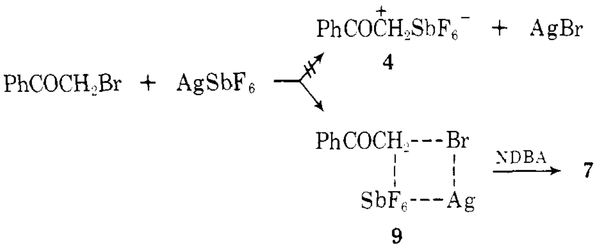


N-nitrene products **5** and **6** coupled with the formation of phenacyl alcohol in 94% yield indicated that intermediate **7** was generated and partially fragmented to **1** thence to **5** and **6** (Scheme I and eq 2). However, the main path was hydrolysis to phenacyl alcohol and NDBA. It was shown in a control experiment that the complex of phenacyl bromide and silver hexafluoroantiomonate, *under the same conditions* (wet ether) but in the *absence* of NDBA, gave phenacyl bromide in nearly quantitative recovery (95%). This suggests that complex **9** and not the phenacyl carbocation is the species that reacts with NDBA and that NDBA must somehow assist in breaking up the complex.



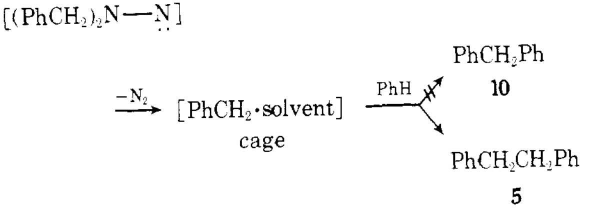
(3)

When benzene was used as solvent, the major product (40–45%) was diphenylmethane (**10**). It was initially believed that benzene was acting as an efficient trap for the benzyl radicals. However, oxidation of 1,1-dibenzylhydrazine in *benzene* with manganese dioxide and with lead tetraacetate gave **5** in 34 and 7% and **6** in 48 and 20% yields, respectively.



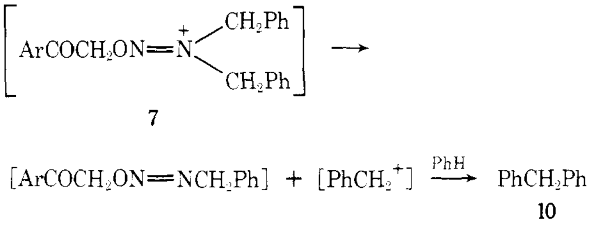
(4)

Similarly, reaction of the anion of 1,1-dibenzylhydrazine with tosyl azide[10] afforded **5** and **6** in 26 and 10% yield; in none of these reactions was diphenylmethane (**10**) detected. The results rule out the reaction of benzyl radical with benzene as the source of diphenylmethane.



(5)

The formation of **10** may be understood in terms of a heterolytic breakdown of **7** to give the benzyl carbocation. Indeed the reaction of benzyl chloride with AgSbF$_6$ in benzene cleanly provided a 95% yield of essentially pure diphenylmethane. Further support for this view came from the reactions of *N*-nitroso-*N*-benzylaniline with phenacyl bromide and AgSbF$_6$ in benzene. Diphenylmethane and biphenyl were obtained in 31 and 10% yields, respectively. The formation of these two compounds must be viewed as arising from heterolytic



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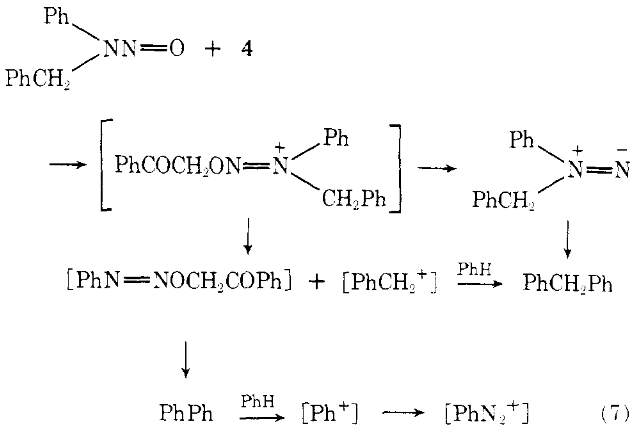
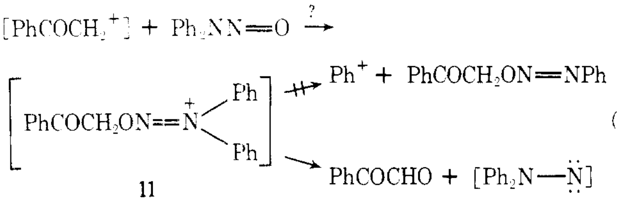


(7)

breakdown as the corresponding *N*-nitrene does *not* undergo homolytic fragmentation to any major extent.[12] The formation of biphenyl from the reaction of phenyl cation with benzene is well documented.[13] In contrast, the reaction of *N*-nitrosodiphenylamine with phenacyl bromide and silver hexafluoroantimonate in benzene gave *no* biphenyl. In this case, the loss of a relatively stable carbocation (eq 8) is not possible even if intermediate **11** is formed. The formation of **11** might not be favored since the substituent phenyl groups may render the nitroso oxygen devoid of any nucleophilic power and thus unable to break up complex **9**. The alternate route, namely loss of an α hydrogen, would also be unfavorable since *N*-diphenylaminonitrene would not easily be formed under these conditions. Even if generated this *N*-nitrene is not known to fragment to phenyl radicals.



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(8)

The absence of the expected arylglyoxals was as puzzling as was the formation of benzils as by-products (experiments 5, 10, and 12). It was surmised that the glyoxals were undergoing further reaction with benzene. This was supported by the report of the formation of benzoins (and their subsequent facile air oxidation to benzils) from the reaction of arylglyoxals with benzene in the presence of aluminum chloride.[14] Indeed the reaction of freshly distilled phenylglyoxal with benzene in the presence of $AgSbF_6$ gave benzil. So far, we are unable to account for the formation of the benzoic acids (experiments 5 and 10). Since *p*-bromobenzoic acid and not benzoic acid was obtained when *p*-bromophenacyl bromide (experiment 10) was used, the benzoic acids evidently arose from the phenacyl component of the reaction.

Experimental Section

All melting points were taken on a Thomas-Hoover Uni-melt apparatus and are uncorrected. Infrared and NMR spectra were recorded on a Perkin-Elmer 137 (Infracord) and Hitachi Perkin-Elmer R-24 spectrometers. VPC analyses were performed on a Perkin-Elmer 154 D fractometer using a stainless steel column packed with silicone grease (20%) on HMDS-CROM W.

Materials. *N*-Nitrosodibenzylamine (NDBA),[15] 1,1-dibenzylhydrazine,[16] and the phenacyl bromides[17] were prepared according to reported procedures. Benzene was purified by a reported method[18] and dried over lithium aluminum hydride. Anhydrous ether, silver hexafluoroantimonate (Alfa Inorganics), and ethyllithium in benzene (Alfa Inorganics) were commercial products and were used as received.

$AgSbF_6$ Induced Reaction of Phenacyl Bromides with NDBA. General Procedure. In Benzene. A mixture of the phenacyl bromide (10 mmol), NDBA (10 mmol), and silver hexafluoroantimonate (10 mmol) in 25 mL of dry benzene was heated to reflux for 24 h with vigorous stirring. Triethylamine (10 mL) was then added to the reaction mixture and heating with stirring was continued for an additional 24 h. The hot reaction mixture was poured into 100 mL of water and the organic layer was washed with water and dilute hydrochloric acid repeatedly. After drying over magnesium sulfate and evaporation of the solvent in vacuo, the resulting dark oil was chromatographed on 50 g of silica gel (60–200 mesh). Rapid elution with *n*-hexane gave diphenylmethane and bibenzyl, identified by comparison with authentic samples. Quantitative analysis of the mixture was performed by NMR and VPC. Further elution with *n*-hexane/benzene and benzene gave benzaldehyde and the more polar fractions. Each product was identified by comparison of its NMR and IR spectra and its VPC retention time with those of authentic samples. Mixture melting points were used also for solid samples.

In the absence of triethylamine, benzoic acid (1.2 mmol) was extracted from the benzene layer with aqueous sodium bicarbonate. Under the same conditions, phenacyl bromides reacted with triethylamine to give the phenacyltriethylammonium bromides. With *p*-bromophenacyl bromide, *p*-bromobenzoic acid (mp 250–252 °C) and 4-bromobenzil (mp 77–80 °C; *m/e* 290, 288) instead of benzoic acid and benzil respectively were obtained in addition to diphenylmethane and bibenzyl. With *p*-nitrophenacyl bromide, 4-nitrobenzil (mp 138–139 °C (lit.[19] mp 140–141 °C); *m/e* 255) was obtained in addition to diphenylmethane and bibenzyl.

In Ether. The procedure was similar to that described above. The reaction mixture was separated and the aqueous layer was extracted with benzene. The combined organic phase was evaporated and the residue was chromatographed. Rapid elution with *n*-hexane gave bibenzyl followed by benzylidenedibenzylhydrazine and benzaldehyde.

Reaction of Phenacyl Bromide, *N*-Nitroso-*N*-benzylaniline, and $AgSbF_6$ in Benzene. The procedure was the same as described for the reaction with NDBA. Chromatography on silica gel gave diphenylmethane (31%), biphenyl (9.7%), benzoic acid (1%), and phenacyl bromide (15%).

Reaction of Phenacyl Bromide, *N*-Nitrosodiphenylamine, and $AgSbF_6$ in Benzene. The procedure described for NDBA was followed. Chromatography of the residue on silica gel gave 65% of the recovered phenacyl bromide but no biphenyl was detected by TLC, IR, or VPC. *N*-Nitrosodiphenylamine when heated to reflux for 24 h gave several compounds (TLC) and diphenylamine in addition to recovered starting nitrosamine.

Oxidation of 1,1-Dibenzylhydrazine in Benzene. With Lead Tetraacetate. To a solution of 1,1-dibenzylhydrazine (10 mmol) in 25 mL of benzene was added portionwise lead tetraacetate (10 mmol) and the mixture was heated to reflux for 20 h with stirring. The precipitated lead diacetate was filtered and the filtrate was washed with water and aqueous sodium bicarbonate repeatedly. The residue obtained from evaporation of the dried benzene solution was chromatographed on silica gel (60–200 mesh, 50 g) and afforded bibenzyl (7%) and benzylidenedibenzylhydrazine (48%) in addition to a liquid (1.03 g) whose IR and NMR spectra indicated it to be mostly benzyl acetate (containing some benzylidenedibenzylhydrazine). There was no substantial difference in the yields of bibenzyl (7.4%) and benzylidenedibenzylhydrazine (41%) and benzyl acetate when 1,1-dibenzylhydrazine was added dropwise to a suspension of lead tetraacetate in benzene at reflux.

With Manganese Dioxide. To a suspension of activated manganese dioxide (1 g) in benzene (25 mL) was added dropwise a solution of 1,1-dibenzylhydrazine (10 mmol) in benzene (25 mL) over a period of 1.5 h and the reaction mixture was then heated to reflux for 20 h with stirring. The precipitated solid was filtered and the filtrate was worked up to give bibenzyl (34%) and benzylidenedibenzylhydrazine (20%).

Reaction of 1,1-Dibenzylhydrazine Anion with Tosyl Azide.[10] Ethyllithium in benzene (10 mL, 1.25 M) was added dropwise to a solution of 1,1-dibenzylhydrazine (10 mmol) in benzene (25 mL) at room temperature over a period of 10 min under a nitrogen atmosphere. Then a solution of tosyl azide (2 g) in benzene (25 mL) was added dropwise at room temperature. After completion of the addition, the reaction mixture was heated to reflux for 2 h, and then quenched by the addition of water. Chromatography of the residue obtained after workup gave bibenzyl (26%) and benzylidenedibenzylhydrazine (10%).

Reaction of Benzyl Chloride with $AgSbF_6$ in Benzene. A mixture of benzyl chloride (10 mmol) and silver hexafluoroantimonate (10 mmol) in 25 mL of benzene was heated to reflux for 24 h with vigorous stirring. The reaction mixture was poured into water and the benzene layer was separated. The aqueous phase was extracted with benzene and the combined organic extract was dried and evaporated to give an oil (1.6 g, 95%) which was characterized as essentially pure diphenylmethane by IR, NMR, VPC, and TLC; no benzyl chloride was present in the oil.

Reaction of Phenacyl Bromide, NDBA, and $AgSbF_6$ in Wet Ether. A mixture of phenacyl bromide (1.92 g, 10 mmol), NDBA (2.26 g, 10 mmol), and silver hexafluoroantimonate (3.5 g, 10 mmol) in wet ether[21] (25 mL) was heated to reflux for 24 h with vigorous stirring. The reaction mixture was poured into water and extracted with benzene. The following compounds were isolated by chromatography of the product with *n*-hexane, varying mixtures of *n*-hexane/benzene and benzene: diphenylmethane (0.39 mmol), benzylidenedibenzylhydrazine (0.21 mmol), benzaldehyde (2.09 mmol), phenacyl bromide (0.48 mmol), NDBA (2.34 mmol) along with unknown products. The fractions eluted with chloroform gave 1.28 g (94%) of phenacyl alcohol, identified by comparison (IR, NMR, TLC) with an authentic sample.[22] Treatment of phenacyl alcohol with *o*-phenylenediamine in methanol gave a 25% yield of 2-phenylquinoxaline, mp 77–78 °C (lit.[23] 77–78 °C).

Reaction of Complex of Phenacyl Bromide and Silver Hexafluoroantimonate with Water. A mixture of phenacyl bromide (1 g, 5 mmol) and silver hexafluoroantimonate (1.8 g, 5 mmol) in anhydrous ether (15 mL) was heated to reflux for 2 h with vigorous stirring. To the reaction mixture was then added water (5 mL) and reflux and stirring were continued for 22 h. The reaction mixture was poured into water and extracted with benzene. The dried benzene extract gave only phenacyl bromide (883 mg, 88.3%).

Reaction of a Complex of Phenacyl Bromide and Silver Hexafluoroantimonate with Benzyl Alcohol. A mixture of phenacyl bromide (1 g, 5 mmol) and silver hexafluoroantimonate (1.8 g, 5 mmol) in anhydrous ether (15 mL) was heated to reflux for 2 h with vigorous stirring. To the reaction mixture was then added benzyl alcohol (5 mL) and reflux and stirring were continued for 22 h. The reaction mixture was poured into water and extracted with benzene. No benzaldehyde was detected on TLC, NMR, and IR.

Reaction of Benzylidenedibenzylhydrazine with $AgSbF_6$ in Wet Ether. A mixture of benzylidenedibenzylhydrazine (1.5 g, 5 mmol) and silver hexafluoroantimonate (1.8 g, 5 mmol) in wet ether[21] (15 mL) was heated to reflux for 24 h with vigorous stirring. The reaction mixture was poured into water and extracted with benzene. Removal of the solvent gave 1.3 g of an oily material which was shown to consist of starting material (89%) and benzaldehyde (11%) by NMR spectral examination.

Reaction of Phenylglyoxal with $AgSbF_6$ in Benzene. A mixture of freshly distilled phenylglyoxal (1.4 g, 10 mmol) and silver hexafluoroantimonate (3.5 g, 10 mmol) in anhydrous benzene was heated to reflux for 24 h with vigorous stirring. The reaction mixture was poured into water and extracted with benzene. The dried benzene extract was evaporated in vacuo and residue was chromatographed on 50 g of silica gel (60–200 mesh). Fractions were eluted rapidly with benzene to give benzil as a thick yellow oil whose IR spectrum and TLC retention time were identical to those of authentic sample; the infrared spectrum of the bis(2,4-dinitrophenylhydrazone), mp 285–290 °C (lit.[24] mp 317–318 °C), was identical to that of an authentic sample.

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Registry No.—NDBA, 5336-53-8; *p*-bromobenzoic acid, 586-76-5; 4-bromobenzil, 39229-12-4; bibenzyl, 103-29-7; benzylidenedibenzylhydrazine, 21136-32-3; benzaldehyde, 100-52-7; diphenylmethane, 101-81-5; 1,1-dibenzylhydrazine, 5802-60-8; benzyl chloride, 100-44-7; phenylglyoxal, 1074-12-0.

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Nitro Displacement by Methanethiol Anion. Synthesis of Bis-, Tris-, Pentakis-, and Hexakis(methylthio)benzenes

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Bis- and tris(methylthio)benzenes have been synthesized by a facile process involving nitro displacement. Also prepared were pentakis- and hexakis(methylthio)benzene. The thioethers were readily oxidized to the corresponding sulfones in high yield.

Nucleophilic displacement of nitro groups either ortho of para to an electron pair stabilizing function is well documented. Our previous reports[1] have demonstrated the synthetic utility of nitro displacement ortho to cyano, carboxylic acid ester, and aldehyde functions by a variety of nucleophiles. Other workers[2] have reported nitro displacement involving activation by sulfone, carboxamide, ketone, and phenyl substituents, in addition to the three functions above. Reports also include displacements starting with 3-nitrophthalic anhydride[3] and *N*-substituted 3-nitrophthalimides.[4]

No examples were found for which the stabilization could be attributed to a thioether function. In fact, Miller[5] reported that *p*-methylthio showed only weak activation (similar to the heavier halogens) in rate studies involving methoxide displacement of chlorine activated by an *o*-nitro group. Also, Bordwell and Boutan[6] predicted only slight electron pair stabilization for an aromatic methylthio substituent based on acidity constants and spectral measurements. In contrast to these reports, we wish to describe several examples of facile nitro displacement by methanethiol anion where the activa-