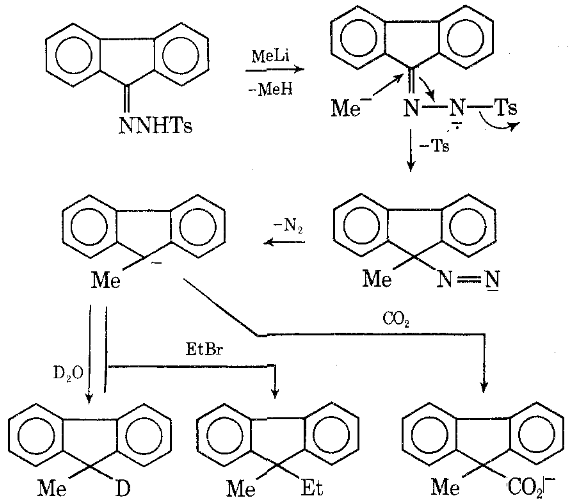

Experimental Section

Fluorenone Tosylhydrazone (I). Fluorenone tosylhydrazone was prepared from fluorenone by the method of Bamford and Stevens.[5] The tosylhydrazone was recrystallized from methanol to give yellow needles, mp 185–186° dec, reported[5] mp 180–182° dec.

9-Methylfluorene. To a solution of fluorenone tosylhydrazone (3.48 g, 0.01 mol) in 50 ml of anhydrous tetrahydrofuran under an atmosphere of nitrogen was added 1.65 *M* methyllithium in ether (Ventron, 18 ml, 0.03 mol) during 5 min. Gas evolved and the solution turned from yellow to deep magenta during the addition. The mixture was stirred at room temperature for 3 hr (gas evolution ceased after ~2 hr) and water was added carefully. The organic phase was washed with saturated sodium chloride solution and dried over calcium chloride. Evaporation of the solvent gave a brown oil which was crystallized from 2-propanol–water as yellow needles, mp 45–46° (reported[6] 45–46°), yield 73%. The mass spectrum showed important peaks at m/e 180 ($M\cdot^+$) and 165 ($M - CH_3$).

9-Methylfluorene-*9-d*₁. Following the procedure for 9-methylfluorene with the exception of decomposing the reaction mixture with D_2O instead of H_2O, we obtained 9-methylfluorene-$9\text{-}d_1$. The pmr spectrum of unlabeled 9-methylfluorene contained a three-proton triplet at 1.5 and a one-proton quartet at 3.9 ppm, whereas that of the labeled compound showed a three-proton singlet at 1.5 and no signal at 3.9 ppm. The mass spectrum showed that this compound contained 94% d_1 (reaction yield 71%).

9-Methyl-9-ethylfluorene. Following the same procedure as above but decomposing the reaction mixture with ethyl bromide (2.18 g, 0.02 mol), we obtained an oil which was crystallized from 2-propanol–water as yellow plates, mp 60–61° (reported[7] 61–62°). The yield was 77%. The pmr spectrum showed a three-proton singlet (9-methyl) at 1.4, a two-proton quartet at 2.0, and a three-proton triplet at 0.4 ppm. The mass spectrum showed important peaks at m/e 208 ($M\cdot^+$), 193 ($M - CH_3$), and 179 ($M - C_2H_5$).

9-Methyl-9-fluorenecarboxylic Acid. Decomposition of the reaction mixture with dry finely divided solid CO_2 gave 9-methyl-9-fluorenecarboxylate, which was dissolved in aqueous sodium hydroxide. After acidification of the aqueous phase with hydrocholoric acid, the free acid separated as an oil. The oil was dissolved in acetic acid and crystallized by the dropwise addition of H_2O to the boiling solution, followed by cooling. The acid separated as pale yellow needles, mp 163–165° (reported[8] 166–167°) in 79% yield. The mass spectrum showed characteristic peaks at m/e 224 ($M\cdot^+$) and 179 ($M - CO_2H$). The 9-methyl group appeared as a singlet in the pmr at 1.8 ppm.

Registry No.—I, 52341-51-2; 9-methylfluorene, 2523-37-7; methyllithium, 917-54-4; 9-methylfluorene-$9\text{-}d_1$, 15480-50-9; 9-methyl-9-ethylfluorene, 42348-903; ethyl bromide, 74-96-4; 9-methyl-9-fluorenecarboxylic acid, 1989-33-9.

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Oxidation of Phenylhydrazine with Nitrosobenzene

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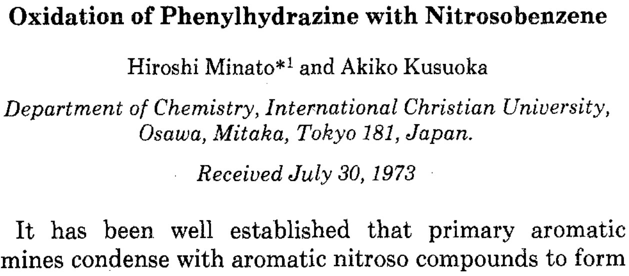
It has been well established that primary aromatic amines condense with aromatic nitroso compounds to form azo compounds. However, the literature about the reaction of phenylhydrazine with nitrosobenzene is conflicting. 1,3-Diphenyltriazene should be the product expected if the reaction is simple condensation between the two with elimination of water. In no case, the formation of 1,3-diphenyltriazene expected was reported. Azobenzene has been reported as the only product when phenylhydrazine is added slowly to a large excess of nitrosobenzene in unheated acetic acid.[2] In another case, *N*-hydroxydiaryltriazenes have been reported to be the major products.[3] In another case, a quantitative gasometric analytical method for *C*-nitroso compounds has been developed according to path c by warming a nitroso compound with an excess of phenylhydrazine in acetic acid.[4] In another case, diarylamine has been reported to be a significant product.[5]



An investigation on this reaction was carried out in our laboratories, and we found that the reaction between nitrosobenzene and phenylhydrazine does not yield 1,3-diphenyltriazene, but the products are azoxybenzene, diphenylamine, benzene, and nitrogen.[6] The mechanism for formation of diphenylamine appeared to be puzzling. A tentative mechanism presented was of ionic nature. Work has been continued, and in this paper we wish to describe the results and propose a modified mechanism involving the phenyl radical.

The products of the reaction between phenylhydrazine and nitrosobenzenes were studied. The samples giving relatively greater yields of diphenylamines are shown in Table I. When a phenylhydrazine solution was added to a nitrosobenzene solution, the yield of diphenylamine was greater; when the order of addition was reversed, the yield was smaller. From the results of the reactions with *p*-nitrosotoluene and *p*-dimethylaminonitrosobenzene, it is clear that one of the two phenyl groups in diphenylamine comes from phenylhydrazine and the other phenyl group comes from nitrosobenzene.

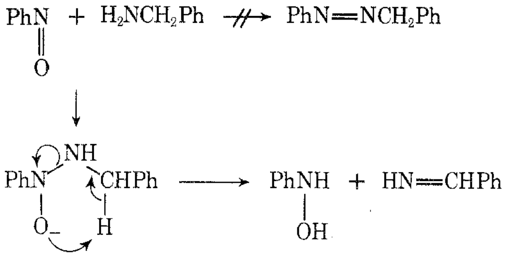
The mechanism of the formation of diphenylamine from the reaction between nitrosobenzene and phenylhydrazine is of interest. Recently Lamson, *et al.*, reported that the reaction of nitrosobenzene with benzylamine did not yield

Table I
Products of the Reactions between Phenylhydrazine and Nitrosoarenes

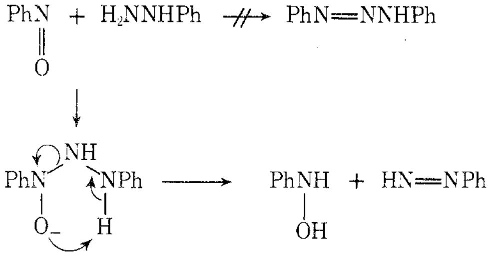
				Products (mol/100 mol ArNO)			
Run	Reactants, mmol	Solvent	Temp, °C	PhNHAr	ArN=NAr	ArN(→O)=NAr	PhH
1	PhNO(9.22) + PhN_2H_3(9.06)	MeOH	−8	13.6	7.6	11.2	*a*
2	PhNO(7.86) + PhN_2H_3(4.41)[b]	MeOH	35	8.4	12.0	22.2	17.0
3	*p*-MeC_6H_4NO(4.77) + PhN_2H_3(4.77)	MeOH	−8	11.6	0	12.8	15.0
4	*p*-$Me_2NC_6H_4NO$(7.46) + PhN_2H_3(7.46)	CH_2Cl_2	−8	10.4	*c*	*c*	*c*

[a] Not determined. [b] At 35°, nitrogen evolved upon addition of each drop of PhN_2H_3 solution, and addition was stopped when no more N_2 evolution was observed. [c] The reaction mixture was tarry, and the identification of other products was not possible.

the expected benzylazobenzene, but yielded phenylhydroxylamine and benzaldimine, which further reacted to form azoxybenzene and *N*-benzylbenzaldimine.[7]



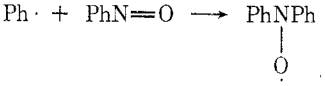
If nitrosobenzene and phenylhydrazine react in a similar manner, phenyldiazene must be produced.



(1)

Huang and Kosower prepared phenyldiazene and showed that it yields phenyl radical by bimolecular reaction with itself.[8] It is also known that phenyl radical adds to nitrosobenzene, forming diphenylnitroxide radical.[9]

$$2\,PhN{=}NH \longrightarrow [PhN{=}N\cdot + Ph\dot{N}NH_2] \longrightarrow Ph\cdot + N_2 \quad (2)$$


(3)

$$Ph\cdot + PhN{=}O \longrightarrow Ph\underset{\underset{\textstyle O}{|}}{N}Ph \quad (3)$$

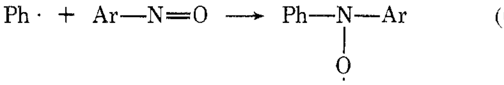
Therefore, if phenyl radical is formed in the reaction between phenylhydrazine and nitrosobenzene, formation of diphenylnitroxide radical is expected, and it is an attractive precursor for diphenylamine.

To check this possibility, benzene solutions of phenylhydrazine and nitrosobenzene were mixed in an esr tube near 0°; the esr spectrum was identical with that of diphenylnitroxide radical reported in the literature.[10] The esr signal remained unchanged as long as the mixture was kept frozen, but quickly disappeared when the mixture was warmed up, probably owing to further reaction with phenylhydrazine and other reactants. Neither a benzene solution of phenylhydrazine nor that of nitrosobenzene showed any esr signals. Only when a benzene solution of phenylhydrazine and that of nitrosobenzene are mixed, strong signals of diphenylnitroxide are observed.

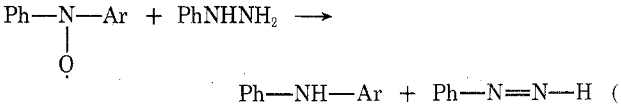
The esr spectrum together with other data obtained suggest that the reactions between phenylhydrazine and nitrosobenzenes are represented by the eq 4–9, involving phenyldiazene and phenyl radical as the intermediates.

$$PhNHNH_2 + Ar{-}N{=}O \longrightarrow Ph{-}N{=}N{-}H + Ar{-}NHOH \quad (4)$$

$$Ph{-}N{=}NH \longrightarrow Ph\cdot + N_2 \quad (5)$$

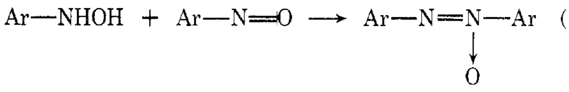


$$Ph\cdot + Ar{-}N{=}O \longrightarrow Ph{-}\underset{\underset{\textstyle O}{|}}{N}{-}Ar \quad (6)$$



$$Ph{-}\underset{\underset{\textstyle O}{|}}{N}{-}Ar + PhNHNH_2 \longrightarrow Ph{-}NH{-}Ar + Ph{-}N{=}N{-}H \quad (7)$$

$$2\,Ar{-}NHOH \longrightarrow Ar{-}N{=}N{-}Ar \quad (8)$$

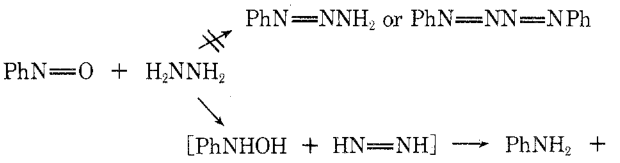


$$Ar{-}NHOH + Ar{-}N{=}O \longrightarrow Ar{-}N{=}\underset{\underset{\textstyle O}{\downarrow}}{N}{-}Ar \quad (9)$$

The eq 8 and 9 are well known, but step 7 must be checked. By use of an authentic diphenylnitroxide sample, the formation of diphenylamine from its reaction with phenylhydrazine was ascertained.

Direct proof of the intermediacy of phenyldiazene is, of course, desirable. The evidence for phenyldiazene presented by Huang and Kosower is ultraviolet-visible spectra, reduction to phenylhydrazine, and volatility. The reaction mixture of our system was strongly colored, and it was not possible to establish the presence of phenyldiazene. Reduction of phenyldiazene to phenylhydrazine is not applicable in our system, since phenylhydrazine is one of the reactants. Isolation of phenyldiazene by distillation was attempted repeatedly, but was unsuccessful.

In a previous paper,[6] we described that the reaction between hydrazine and nitrosobenzene does not yield phenyltriazene, but aniline and nitrogen with some azobenzene. The present results suggest that the reaction between hydrazine and nitrosobenzene proceeds *via* diimide as an intermediate.



Experimental Section

Materials. Nitrosobenzene,[11] *p*-nitrosotoluene,[11] and *p*-dimethylaminonitrosobenzene[12] were prepared according to the methods described in the literature.

Reaction between a Nitrosoarene and Phenylhydrazine. Run 1. When phenylhydrazine (9.22 mmol) in methanol (80 ml) was added to a green solution of nitrosobenzene (9.06 mmol) in methanol (10 ml) at −8°, the solution turned yellowish green, but no evolution of nitrogen was observed. When the solution was slowly warmed up, evolution of nitrogen started at −2°. After the reaction was completed at room temperature, the solvent was distilled off, and the dark reddish oil obtained was subjected to elution chromatography. The first fraction (orange needles) was azobenzene, the second (yellow crystals) was azoxybenzene, and the third (white crystals) was diphenylamine. Identification of the products was made on the basis of their mp and comparison of their ir and nmr spectra with those of the authentic samples.

The procedures for other runs were essentially similar to that described above. When the two reactants were mixed at 35°, nitrogen evolved instantaneouly. Benzene was always one of the products formed, but its amount was not always determined.

Esr Measurement of Diphenylnitroxide Radical. A benzene solution (1.1 g) of nitrosobenzene (0.02 g) was cooled to 0° in an esr tube, and before it solidified a benzene solution (0.45 g) of phenylhydrazine (0.03 g) was added. Its esr spectrum was determined at 0° with a JES-PE esr spectrometer. The signals of diphenylnitroxide radical were observed,[10] and did not change as long as the mixture was kept as solid at 0°. When it was warmed up and melted, the signals of the radical disappeared ($g = 2.0057$, $a^N = 10.0$ G). When a benzene solution of nitrosobenzene or that of phenylhydrazine was subjected to esr measurements, no esr signals were observed. Only when the two solutions were mixed, were esr signals of diphenylnitroxide radicals observed.

Reaction between Diphenylnitroxide and Phenylhydrazine. A methanol solution (25 ml) of diphenylnitroxide (0.4 g, 2.3 mmol) was cooled to −5°, and then a methanol solution (3 ml) of phenylhydrazine (0.1 g, 0.92 mmol) was added to the cooled solution. The dark red solution became yellow with evolution of some nitrogen. After the mixture was warmed to and allowed to stand at room temperature for 1 hr, the solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography (alumina). The first fraction eluted with hexane–benzene (3:2) was rechromatographed with hexane, and the first fraction eluted was identified as diphenylamine by comparison of its ir spectrum with that of an authentic sample; yield, 0.046 g (0.12 mol/mol of Ph_2NO used).

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Registry No.—Phenylhydrazine, 100-63-0; nitrosobenzene, 586-96-9; *p*-nitrosotoluene, 623-11-0; *p*-dimethylaminonitrosobenzene, 138-89-6; diphenylnitroxide, 712-51-6.

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Intramolecular Migration of the Pentafluorophenyl Group under Acidic Conditions

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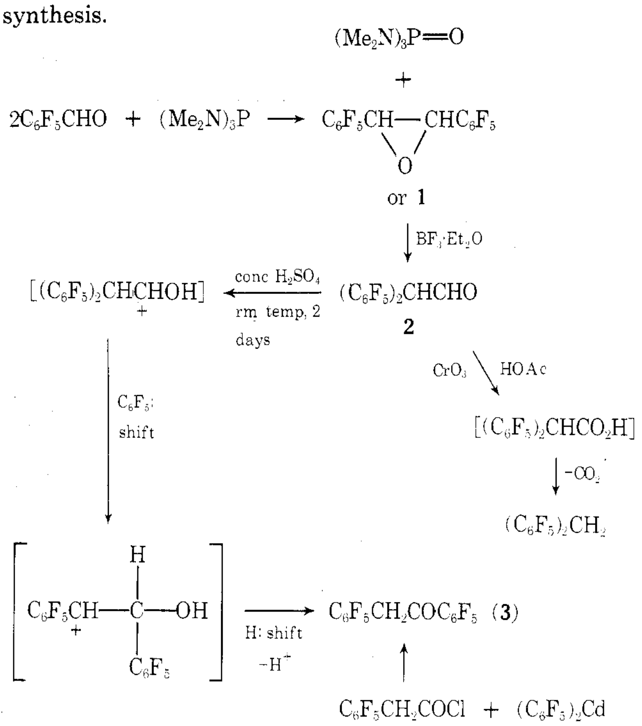
Acid-catalyzed skeletal rearrangements involving the 1,2 shift of aryl groups are well known. Phenyl groups containing electron-attracting substituents generally migrate much more slowly than phenyl, if at all. One might anticipate that the moderately electron-withdrawing pentafluorophenyl group[2a] would cause considerable deactivation in such reactions. To our knowledge, acid-catalyzed rearrangements involving intramolecular 1,2 migration of the C_6F_5 group have not been reported. We describe here a series of interrelated reactions in which we observed such aryl participation.

Pentafluorobenzaldehyde reacted rapidly with tris(dimethylamino)phosphine (hexamethylphosphorus triamide) to give a mixture of diastereomeric stilbene oxides.[2b] This mixture or the pure *trans*-stilbene oxide (**1**), obtained by peroxidation of the olefin,[3] reacted with boron trifluoride etherate to form the isomeric decafluorodiphenylacetaldehyde (**2**) by migration of the C_6F_5 moiety. Compound **2** was oxidized by Jones reagent to the diphenylacetic acid which rapidly lost CO_2 to form decafluorodiphenylmethane. When treated with concentrated H_2SO_4, **2** slowly underwent a reverse, 1,2-pentafluorophenyl shift *via* the unstable cation **4**,[4] to give the isomeric ketone (**3**), whose structure was confirmed by independent synthesis.



In order to compare the relative migratory aptitudes of the phenyl and pentafluorophenyl groups, the unsymmetrical stilbene **5**, prepared by Wittig syntheses ($C_6F_5CH_2Br$ and PhCHO or $PhCH_2Br$ and C_6F_5CHO), was converted to the epoxide **6**, which was isomerized to the diphenylacetaldehyde **7**. Compound **7** was characterized by its infrared spectrum and 2,4-dinitrophenylhydrazone. The latter reaction provides no information on which aryl group migrated. However, on standing with concentrated H_2SO_4 at room temperature, **7** was readily transformed into the ketone **8** in a 95% conversion with no evidence of the presence of its isomer, $PhCH_2COC_6F_5$. Also, compound **8** readily formed a 2,4-dinitrophenylhydrazone, showed carbonyl absorption around 1700 cm^{-1}, and was in all respects identical with an authentic sample (*cf.* isomer, Experimental Section). This observation demonstrated the strong preference of C_6H_5 over C_6F_5 migration in such 1,2 shifts. Ketone **8** was also prepared by two alternate routes, one of which has been reported previously.[5] These results are in marked contrast to the overwhelming migratory preference of C_6F_5 over C_6H_5 in 1,2 shifts in alkaline medium.[6] In the latter case, the