HCl were charged into a 25-ml round-bottomed flask equipped with a reflux condenser and a magnetic stirring unit. The mixture was stirred and heated at 100° for 2 hr. The bottom organic layer crystallized after the two-phase mixture had cooled to give 0.7 g (95%) of trichloroacetanilide, mp 93–94° after two recrystallizations from ethanol (lit.[27] mp 94–95°).

1-Phenyl-2,2,3,3-tetrachloroaziridine was not hydrolyzed under these conditions and was recovered unchanged.

Reactions of Phenyl(bromodichloromethyl)mercury with Azobenzene and Azoxybenzene. A 50-ml flask equipped with a thermometer, magnetic stir bar, and a condenser topped with a nitrogen inlet tube was charged with the azobenzene or azoxybenzene and the mercurial. The reaction was carried out either at room temperature in benzene solution or in refluxing benzene solution. The resulting reaction mixture was dark red-brown in color. The crude PhHgBr, obtained as a brown solid in 80–90% yield, decomposed at 230° to give a black tar. The filtrate was directly analyzed with an MIT isothermal unit or was trap-to-trap distilled at 0.02 mm (pot temperature to 100°). The distillate was examined by glc (F & M Model 700 gas chromatograph using a 4 ft × 0.25 in. column, 10% UC W-98 at 130–150°, *n*-hexadecane as internal standard). Products were isolated by glc and identified by the comparison of their ir spectrum and glc retention time with those of the authentic samples synthesized independently. The results are summarized in Table II.

Acknowledgments. The authors are grateful to the U. S. Air Force Office of Scientific Research (NC)-AFSC (Grant AF-AFOSR-72-2204) for generous support of this work and to M & T Chemicals, Inc., for gifts of chemicals.

Registry No. Phenyl(bromodichloromethyl)mercury, 3294-58-4; phenylbenzimidoyl chloride, 4903-36-0; 1,3-diphenyl-2,2,3-trichloroaziridine, 42880-67-1; diphenyldichloroacetimidoyl chloride, 42880-68-2; phenyltrichloroacetimidoyl chloride, 25252-86-2; *N*-benzylideneaniline, 538-51-2; 1,2-diphenyl-3,3-dichloroaziridine, 3543-98-4; cyclohexyltrichloroacetimidoyl chloride, 25252-87-3.

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Aziridines. 27. The Synthesis and Reactions of 4-Aroyltetrahydro-2*H*-1,2,4-oxadiazines

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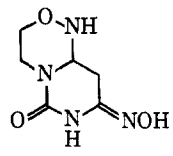
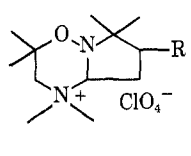
2-Aryl- or 2-alkyl-4-aroyltetrahydro-2*H*-1,2,4-oxadiazines have been prepared by heating 1-aroylaziridines and nitrones in toluene or *m*-xylene. In hot acetic acid 2-(*p*-tolyl)-3-phenyl-4-(3,5-dinitrobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (**6**) is converted into a mixture of *p*-azotoluene, *p*-azoxytoluene, benzaldehyde and *N*-(β-hydroxyethyl)-3,5-dinitrobenzamide. **6** reacts with *p*-nitrotoluene in concentrated sulfuric acid to give 2-methyl-5-nitro-4′-aminodiphenylmethane, *N*-(β-hydroxyethyl)-3,5-dinitrobenzamide, and benzaldehyde. In hot basic solution 2-(*p*-tolyl)-3-phenyl-4-(*p*-nitrobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (**5**) isomerizes into *N*-(*p*-tolyl)-β-(*p*-nitrobenzamido)ethylbenzimidate (**17**). Reduction of **6** leads to *N*-benzyl-*p*-toluidine and thermolysis of **6** at 200° causes vigorous decomposition and formation of *N*-benzal-*p*-toluidine.

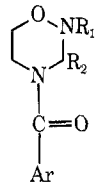
Only a limited number of saturated 1,2,4-oxadiazines are known. Those that have been reported include the dihydrocytosine derivative **1**[1] and the 1,2,4-oxadiazinium salts **2**. The salts **2** were prepared by treating aziridinium perchlorates with cyclic nitrones.[2,3] In view of this reaction and the known ring-opening reactions of 1-carbethoxy- and 1-aroylaziridines by dipolar species such as enamines,[4] phosphonium and arsonium ylides,[5,6] and dimethyl sulfoxide,[7] it seemed likely that nitrones would interact with 1-aroylaziridines to produce 4-aroyltetrahydro-2*H*-1,2,4-oxadiazines (**3**). The purpose of this paper is to describe the synthesis of **3** and to delineate the reactions



1



2



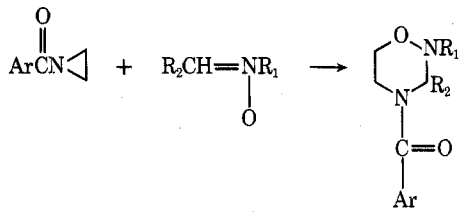
3

of **3** with glacial acetic acid, sulfuric acid, reducing reagents, and potassium hydroxide in dimethylformamide (DMF).

Results and Discussion

4-Aroyltetrahydro-2*H*-1,2,4-oxadiazines (3) were usually obtained when a mixture of a nitrone and an 1-aroylaziridine was refluxed in toluene or *m*-xylene (Scheme I, Table I).

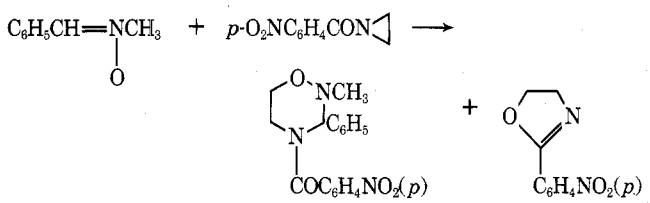
Scheme I



3

In a few instances heating a mixture of a nitrone and an 1-aroylaziridine produced little or no 3. In these cases, an isomer of the 1-aroylaziridine, namely an 2-aryl-2-oxazoline, was formed. For example, heating α-phenyl-*N*-methylnitrone with 1-(3,4-dichlorobenzoyl)aziridine or with 1-(*p*-nitrobenzoyl)aziridine gave 2-(3,4-dichlorophenyl)-2-oxazoline (45%) and 2-(*p*-nitrophenyl)-2-oxazoline (80%), respectively. In the former case no 1,2,4-oxadiazine was isolated and in the latter case only 7% of 2-methyl-3-phenyl-4-(*p*-nitrobenzoyl)-tetrahydro-2*H*-1,2,4-oxadiazine (13) was obtained (Scheme II). In sharp contrast, the same nitrone reacted with 1-(3,5-dinitrobenzoyl)-aziridine to give only 2-methyl-3-phenyl-4-(3,5-dinitrobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (7) in 73% yield.

Scheme II



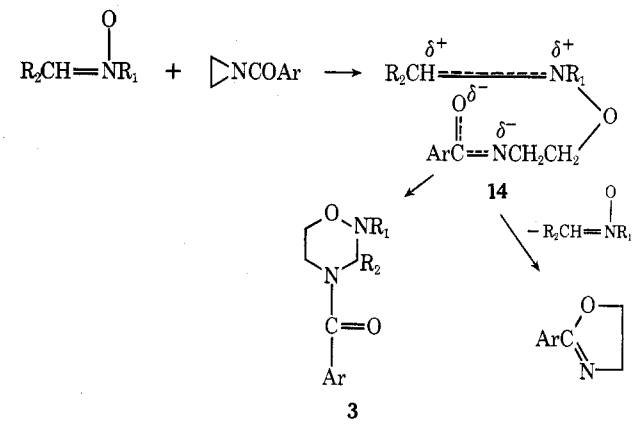
13

The mass spectra of the 4-aroyltetrahydro-2*H*-1,2,4-oxadiazines (3) were consistent with the structural assignments. Thus, the mass spectrum of 2,3-diphenyl-4-(*p*-nitrobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (4) exhibited peaks at *m/e* 389 (molecular ion, $C_{22}H_{19}N_3O_4$), 359 ($M^+ - H_2CO$), 181 ($C_6H_5N{=}CHC_6H_5$), 180 ($C_6H_5N{\equiv}CC_6H_5$), and 150 ($O_2NC_6H_4CO$). Corresponding fragments were obtained for compounds 7 and 10.

The nmr spectra of 3 usually showed the methylene groups as a broad multiplet extending (in the case of 4) from δ 3.2 to 4.4. The proton at C-3 appeared in the aromatic region for all of the 1,2,4-oxadiazines substituted with aryl groups in the 2 and 3 positions of the ring. For those 1,2,4-oxadiazines substituted with a methyl group at position 2 the C-3 proton appeared further upfield.

A mechanism that could account for both the formation of the 1,2,4-oxadiazines and the 2-aryl-2-oxazolines involves a nucleophilic attack of the nitrone oxygen on the aziridinyl carbon to form the dipolar intermediate 14 which then could either ring close to 3 or expel nitrone to give the isomeric 2-oxazoline (Scheme III). That the isomerization of 1-aroylaziridines into 2-aryl-2-oxazolines is catalyzed by a nitrone is not to be entirely unexpected. Dipolar species such as triphenylphosphonium phenacylides have been observed to catalyze this reaction[6] and it is well documented that nucleophiles such as iodide ion, thiocyanate ion, and tertiary amines are effective catalysts for this isomerization.

Scheme III

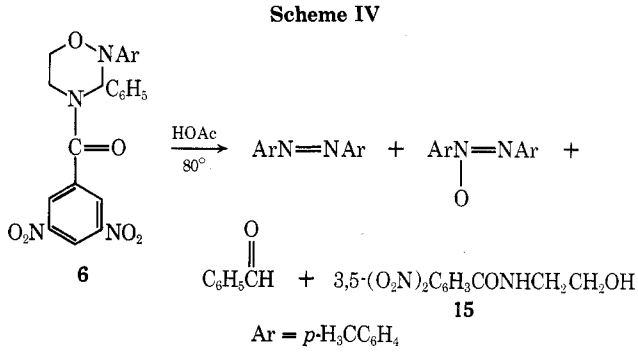


3

The factors determining whether intermediate 14 forms an 1,2,4-oxadiazine or displaces a nitrone to give an 2-oxazoline are subtle. 1,2,4-Oxadiazine formation involves bonding between the positive and negative centers of 14 while 2-oxazoline formation involves a nucleophilic displacement at a saturated carbon atom. The latter reaction would depend in part on the nucleophilicity of the ambident benzamido group of 14 and in part on the ability of the incipient nitrone moiety incorporated in 14 to act as a leaving group. More nitrone character would be imparted to 14 if R_1 were methyl rather than aryl since the methyl group can more effectively reduce the positive charge on the adjacent carbon atom than an aryl group. This would favor nitrone displacement from 14. Such seems to be the case when α-phenyl-*N*-methylnitrone reacted with 1-(3,4-dichlorobenzoyl)- and 1-(*p*-nitrobenzoyl)aziridines. That this same nitrone reacted with 1-(3,5-dinitrobenzoyl)aziridine to give the 1,2,4-oxadiazine 7 in high yield rather than 2-oxazoline may be attributed to the low nucleophilicity of the negatively charged 3,5-dinitrobenzamido group of 14.

Reactions of 4-Aroyltetrahydro-2*H*-1,2,4-oxadiazines. When 2-(*p*-tolyl)-3-phenyl-4-(3,5-dinitrobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (6) was placed in glacial acetic acid and the solution was warmed to 80°, a mixture of *p*-azotoluene (50%), *p*-azoxytoluene (33%), *N*-(β-hydroxyethyl)-3,5-dinitrobenzamide (15, 60%), and benzaldehyde (57%) was produced (Scheme IV).

Scheme IV



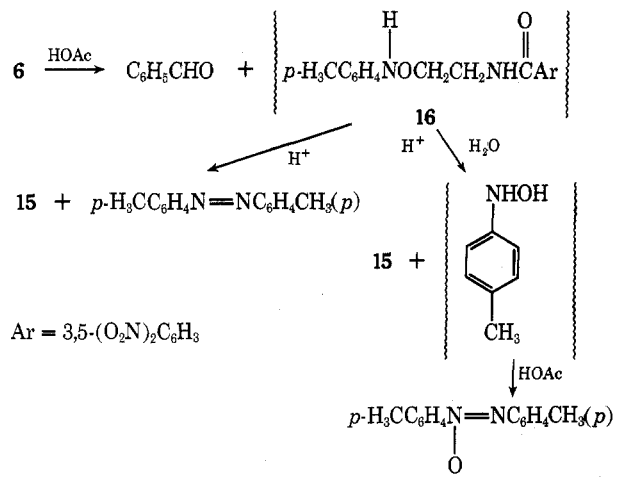
6

Ar = *p*-$H_3CC_6H_4$

Under similar conditions compound 10 formed *p*-azotoluene (37%), *p*-azoxytoluene (4%), *N*-(β-hydroxyethyl)-3,4-dichlorobenzamide (71%), and benzaldehyde (33%).

These products may arise from an acid-catalyzed hydrolysis of 6 to benzaldehyde and intermediate 16 (Scheme V). Hydrolysis of 16 would yield 15 and *N*-(*p*-tolyl)hydroxylamine, which under the reaction conditions employed would be converted into *p*-azoxytoluene (Scheme V). A control run of *N*-(*p*-tolyl)hydroxylamine in glacial acetic acid at 80° gave *p*-azoxytoluene in 95% yield. The autoxidation of phenylhydroxylamines to azoxy-

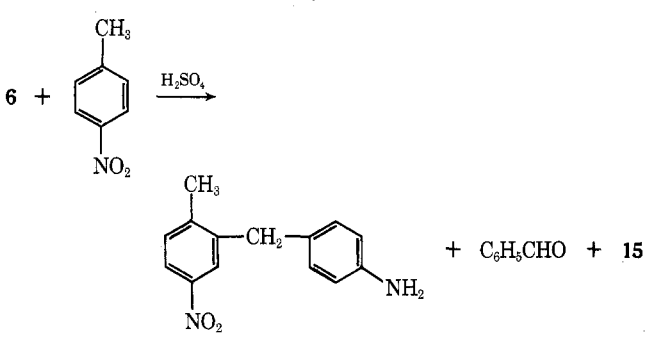
Scheme V



benzenes was observed over 70 years ago by Bamberger[8] and recently the kinetics of this transformation were studied.[9] The *p*-azotoluene (and some of **15**) may also arise from intermediate **16**. Thus, we have observed that when *O*-methyl-*N*-(2,4-dinitrophenyl)hydroxylamine was refluxed in glacial acetic acid, 2,2′,4,4′-tetranitroazobenzene was formed in 35% yield. Similarly, *O,N*-di(5-methyl-2,4-dinitrophenyl)hydroxylamine, when heated in acetic anhydride, gave 5,5′-dimethyl-2,2′,4,4′-tetranitroazobenzene.[10] Control runs in glacial acetic acid at 80° have established that *p*-azotoluene is not converted into *p*-azoxytoluene nor is *p*-azoxytoluene converted into *p*-azobenzene under these conditions.

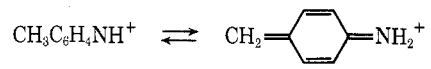
Dissolution of oxadiazines **5**, **6**, and **10** (Table I) in concentrated sulfuric acid at room temperature gave benzaldehyde (isolated as its 2,4-dinitrophenylhydrazone) in high yield. Oxadiazine **11**, similarly treated, gave *p*-chlorobenzaldehyde. No other products were isolable under these reaction conditons. However, when *p*-nitrotoluene was dissolved with an oxadiazine such as **6** in concentrated sulfuric acid, the products 2-methyl-5-nitro-4′-aminodiphenylmethane, *N*-(β-hydroxylethyl)-3,5-dinitrobenzamide (**15**), and benzaldehyde were obtained in 83, 53, and 37% yields, respectively (Scheme VI). Similarly, a mix-

Scheme VI



ture of *p*-nitrotoluene and 2-(*p*-tolyl)-3-phenyl-4-(3,4-dichlorobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (**10**) in concentrated sulfuric acid gave 2-methyl-5-nitro-4′-aminodiphenylmethane, *N*-(β-hydroxyethyl)-3,4-dichlorobenzamide, and benzaldehyde in 73, 20, and 80% yields, respectively. When a mixture of **6** and *p*-nitroanisole was added to concentrated sulfuric acid, 2-methoxy-5-nitro-4′-aminodiphenylmethane (82%) was obtained.

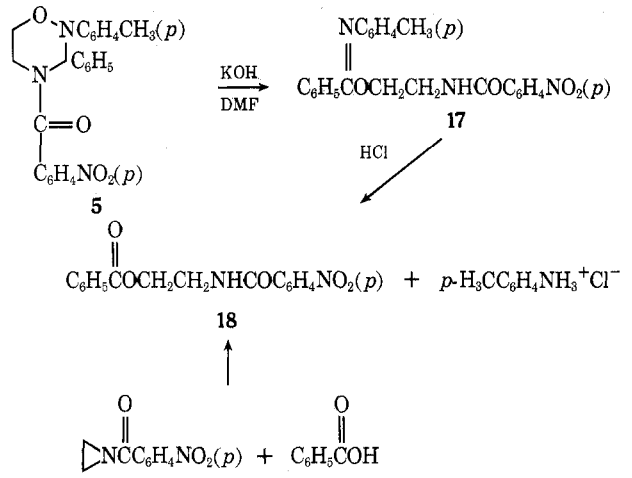
The reaction of **6** with *p*-nitrotoluene in sulfuric acid could also arise by acid hydrolysis of **6** to benzaldehyde, *N*-(*p*-tolyl)hydroxylamine, and **15**. The *N*-(*p*-tolyl)hydroxylamine, as previously shown by Bamberger,[11] then interacts with *p*-nitrotoluene in the presence of concentrated sulfuric acid to give 2-methyl-5-nitro-4′-aminodiphenylmethane. Presumably the *N*-(*p*-tolyl)hydroxylamine reacts with the concentrated sulfuric acid to give an electron-deficient nitrogen species such as the tautomeric nitrenium ion



which then condenses with the *p*-nitrotoluene. It is even likely that intermediate **16** (Scheme V) in concentrated sulfuric acid forms **15** and the nitrenium ion $H_3CC_6H_4NH^+$ directly. Bamberger had also reported that *p*-tolylazide with *p*-nitrotoluene in sulfuric acid gave 2-methyl-5-nitro-4′-aminodiphenylmethane,[12] probably through the intermediacy of the same nitrenium ion.

Treatment of **5** with potassium hydroxide in dimethylformamide gave the benzimidate **17** in 81% yield (Scheme VII). Evidence for the structure of **17** was obtained by hydrolyzing it in dilute hydrochloric acid. The products were *p*-toluidine hydrochloride and β-(*p*-nitrobenzamido)ethyl benzoate (**18**, 83%, Scheme VII). The latter compound

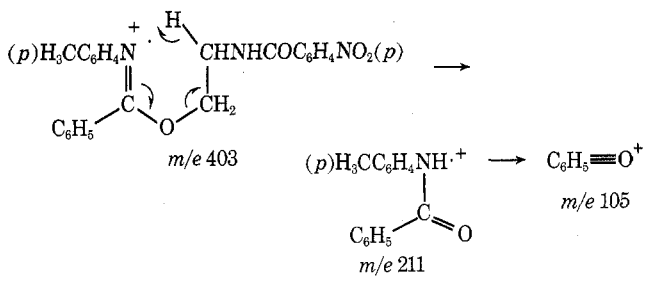
Scheme VII



was also prepared by refluxing benzoic acid and 1-(*p*-nitrobenzoyl)aziridine in chloroform. The reaction of carboxylic acids with 1-acylaziridines is a known synthetic method for the preparation of compounds akin to **18**.[13]

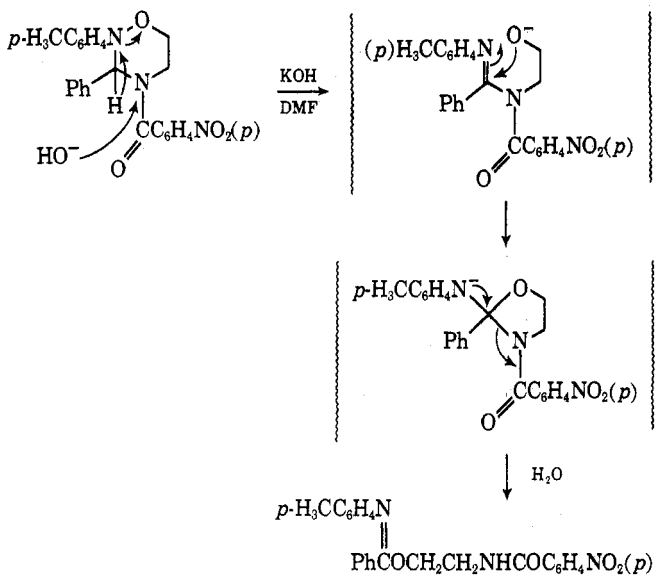
Corroborative evidence for the structure of **17** was obtained from its mass spectrum. The primary fragmentation pathway is a rearrangement of the molecular ion (*m/e* 403) with charge localization on nitrogen, giving *m/e* 211, which in turn cleaves to give a benzoyl ion at *m/e* 105 (Scheme VIII).

Scheme VIII



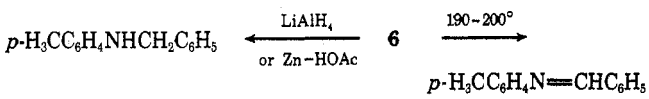
A plausible mechanism for the rearrangement of **5** to **17** is shown in Scheme IX.

Scheme IX



Reduction of the 1,2,4-oxadiazine derivative **6** with either lithium aluminum hydride or zinc–acetic acid produced *N*-benzyl-*p*-toluidine (Scheme X). **6** or **10** decomposed vigorously at 190–200° to give tar and *N*-benzal-*p*-toluidine.

Scheme X



Experimental Section

Materials. 1-*p*-(Nitrobenzoyl)aziridine,[14] 1-(3,5-dinitrobenzoyl)-aziridine,[14] and 3,4-dichlorobenzoylaziridine[15] were prepared as described previously. The nitrones were prepared by reaction of N-substituted hydroxylamines with aldehydes according to literature procedures[16,17] and were known compounds.

4-Aroyltetrahydro-2*H*-1,2,4-oxadiazines (4–13). Equimolar quantities (1–10 mmol) of nitrone and 1-aroylaziridine were added to either dry toluene or *m*-xylene in the ratio of 10 ml of solvent for every millimole of 1-aroylazidine employed. Toluene was the solvent of choice for the preparation of compounds **4–7** and **10–12** and *m*-xylene for compounds **8**, **9**, and **13**. The reaction mixture was refluxed for the specified time (Table I) and then the solvent was evaporated. On occasion, unreacted starting material precipitated from the cool reaction mixture and it was filtered prior to the evaporation of the solvent. The residue was triturated with ether except in the cases of **8** and **13**, which were triturated with methanol and 95% ethanol, respectively. The crude 1,2,4-oxadiazine was filtered. Compounds **4**, **5**, **8**, **9**, and **13** were recrystallized from 95% ethanol; compounds **6** and **12** were recrystallized from acetonitrile; compounds **7** and **10** were recrystallized from butanone.

Reactions of 2-(*p*-Tolyl)-3-phenyl-4-(3,5-dinitrobenzoyl)tetrahydro-2*H*-1,2,4-oxadiazine (6) in Acetic Acid. A mixture of 1.006 g (2.24 mmol) of **6**, 15 ml of glacial acetic acid, and 4 drops of water was stirred at 80° for 2 hr. The dark red reaction mixture was poured onto 10 g of ice with vigorous stirring. A yellow solid precipitated (0.182 g) and was filtered. The filtrate was saved. An infrared spectrum of the solid revealed that it was a mixture of *p*-azotoluene and *p*-azoxytoluene. An analysis of the nmr spectrum showed that the mixture was 58% *p*-azotoluene and 42% *p*-azoxytoluene, which corresponds to an overall yield of 50% *p*-azotoluene and 33% *p*-azoxytoluene. A mixture composed of 58% authentic *p*-azotoluene and 42% *p*-azoxytoluene gave a nmr spectrum virtually identical with that of the crude product. Three recrystallizations of the crude product gave *p*-azotoluene, mp 139–144°.

The filtrate was extracted with three 25-ml portions of petroleum ether (bp 30–60°) to remove any benzaldehyde that formed. The aqueous layer was evaporated and the residue was extracted with 30 ml of hot water. Evaporation of the water gave 340 mg (60%) of crude *N*-(β-hydroxyethyl)-3,5-dinitrobenzamide (**15**) which was identified by comparison of its ir spectrum with that of an authentic sample.[18] Four recrystallizations from water gave **15**, mp 139–145° (lit. mp 146°).

In another run, 1.007 g of **6** in 15 ml of acetic acid was heated at 80° for 6 hr. The mixture was poured on ice and the precipitate (azotoluene and *p*-azoxytoluene) was filtered. To the filtrate was added an excess of a solution of 2,4-dinitrophenylhydrazine. The precipitate of benzaldehyde 2,4-dinitrophenylhydrazone was filtered and weighed 363 mg (57%). It was identified by melting point and infrared spectroscopy.

Reaction of 6 with *p*-Nitrotoluene in Concentrated Sulfuric Acid. In a 10-ml erlenmeyer flask equipped with a magnetic stirring bar were added 500 mg (3.8 mmol) of *p*-nitrotoluene and 510 mg (1.14 mmol) of **6**. The flask was immersed in an ice bath and 5 ml of concentrated H_2SO_4 was added with stirring. After 11 hr at room temperature, the mixture was poured onto 10 g of ice. The yellow precipitate that formed was filtered and the filtrate was saved. The solid was washed with three 15-ml portions of boiling petroleum ether (bp 30–60°) to remove unreacted *p*-nitrotoluene. The yellow residue was triturated with 20 ml of a 5% solution of sodium carbonate solution (foaming occurred) and then filtered. The crude 2-methyl-5-nitro-4′-aminodiphenylmethane weighed 230 mg (83%) and after several recrystallizations from aqueous ethanol melted at 120–122° (lit.[13,19] mp 117–118°). The ir spectrum of the product was identical with that of an authentic sample.[19]

The initial filtrate that was saved was extracted with four 20-ml portions of petroleum ether (bp 60–100°). To the petroleum ether extract was added an excess of a 1% ethanolic 2,4-dinitrophenylhydrazine solution. The benzaldehyde 2,4-dinitrophenylhydrazone that precipitated was filtered and weighed 106 mg (37%). The aqueous layer from the petroleum ether extraction was neutralized with 3 *M* NaOH and extracted with four 25-ml portions of $CHCl_3$. Evaporation of the chloroform gave 152 mg (53%) of crude *N*-(β-hydroxyethyl)-3,5-dinitrobenzamide (**15**) which melted after one recrystallization from water at 138–141° (lit.[18] mp 146°). The infrared spectrum of **15** was identical with that of an authentic sample.[18]

Table I[a]
4-Aroyltetrahydro-2*H*-1,2,4-oxadiazines Prepared by Reaction of 1-Aroylaziridines with Nitrones

	ArCONCH(R₂)N(R₁)OCH₂CH₂							
Compd	Ar	Aziridine registry no.	R_2	R_1	Nitrone registry no.	Crude yield, %	Mp, °C	Reaction time, hr
4	*p*-$O_2NC_6H_4$	19614-29-0	C_6H_5	C_6H_5	1137-96-8	51	147–150	65
5	*p*-$O_2NC_6H_4$		C_6H_5	*p*-$H_3CC_6H_4$	19064-77-8	88	157–160	16
6	3,5-$(O_2N)_2C_6H_3$	42790-32-9	C_6H_5	*p*-$H_3CC_6H_4$		99	190–191	3
7	3,5-$(O_2N)_2C_6H_3$		C_6H_5	CH_3	3376-23-6	73	133–134	0.33
8	3,5-$(O_2N)_2C_6H_3$		CH_3	C_6H_{11}	3376-30-5	27	123–125	0.05
9	*p*-$O_2NC_6H_4$		C_6H_5	$(H_3C)_3C$	3376-24-7	44	186–188	9
10	3,4-$(Cl)_2C_6H_3$	15257-82-6	C_6H_5	*p*-$H_3CC_6H_4$		78	135–138	22
11	3,5-$(O_2N)_2C_6H_3$		*p*-ClC_6H_4	*p*-$H_3CC_6H_4$	37056-74-9	84	218–221	0.75
12	3,5-$(O_2N)_2C_6H_3$		C_6H_5	*p*-$H_5C_2C_6H_4$	42790-35-2	66	182–183	1.5
13	*p*-$O_2NC_6H_4$		C_6H_5	CH_3		6.6	106–109	4.5

[a] Satisfactory analytical data for C, H, and N were reported for all new compounds listed in the table.

Reaction of 10 with p-Nitrotoluene in Concentrated Sulfuric Acid. Using the same procedure described above for **6**, a mixture of 450 mg (1.02 mmol) of **10** and 500 mg (3.8 mmol) of *p*-nitrotoluene and 5 ml of concentrated H_2SO_4 gave 2-methyl-5-nitro-4′-aminodiphenylmethane (73%) and benzaldehyde (80%). The aqueous layer obtained after extracting the benzaldehyde with petroleum ether was extracted with ether instead of chloroform to give 46 mg (20%) of *N*-(β-hydroxyethyl)-3,4-dichlorobenzamide, mp 146–149°. The infrared spectrum was identical with that of an authentic sample of *N*-(β-hydroxyethyl)-3,4-dichlorobenzamide obtained by hydrolyzing 1-(3,4-dichlorobenzoyl)aziridine.

Reaction of 6 with p-Nitroanisole in Concentrated Sulfuric Acid. A mixture of **6** (300 mg, 0.67 mmol) and *p*-nitroanisole (300 mg, 0.78 mmol) was treated in sulfuric acid by the procedure described above for **6** and *p*-nitrotoluene. After stirring for 3 hr at room temperature, the reaction mixture was poured onto 5 g of ice and filtered. The filter cake was triturated with three 20-ml portions of a 1:1 solution of petroleum ether (bp 30–60°) and ether to remove the unreacted *p*-nitroanisole and the resulting suspension was filtered. The crude product was treated with 20 ml of 5% Na_2CO_3 and filtered to give 142 mg (82%) of 2-methoxy-5-nitro-4′-aminodiphenylmethane. The product was recrystallized from 95% ethanol, mp 146–148°.

Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 65.00; H, 5.58; N, 10,83.

No attempts were made to isolate any other products from this reaction.

2,2′,4,4′-Tetranitroazobenzene. A mixture of 600 mg (2.82 mmol) of *O*-methyl-*N*-(2,4-dinitrophenyl)hydroxylamine[20] and 15 ml of glacial acetic acid was refluxed for 20 hr. The reaction mixture was poured on ice and the crude 2,2′,4,4′-tetranitroazobenzene (177 mg, 35%) was filtered. Identification was made by comparison of its ir spectrum with that of an authentic sample.[21]

Conversion of 5 to 17. To a mixture of 100 mg (0.247 mmol) of **5** and 1.5 ml of dry DMF was added 15 mg of powdered KOH. After stirring for 2.5 hr, water was added to the reaction mixture until the final volume was 10 ml. Acetonitrile (3 ml) was added and the oily precipitate was triturated. The crude **17** (81 mg, 81%) was filtered and recrystallized from aqueous ethanol, mp 125–127°, molecular ion *m/e* 403.

Anal. Calcd for $C_{23}H_{21}N_3O_4$: C, 68.48; H, 5.25; N, 10.42. Found: C, 68.64; H, 5.27; N, 10.32.

Hydrolysis of 17 to 18 and p-Toluidine Hydrochloride. A mixture of 100 mg (0.427 mmol) of **17** and 5 ml of 6 *N* hydrochloric acid was heated to 90° for 5 min. The crude **18** was filtered from the hot reaction mixture and the filtrate was saved. The crude **18** (65 mg, 83%) melted after recrystallization from aqueous ethanol at 143–145° (lit.[22] mp 145–146°). An infrared spectrum of **18** was identical with that of an authentic sample. The filtrate was evaporated and the *p*-toluidine hydrochloride was identified by infrared spectroscopy.

Reduction of 6 by $LiAlH_4$. A mixture of 50 mg (1.32 mmol) of $LiAlH_4$ and 20 ml of dry tetrahydrofuran was refluxed for 15 min. To this mixture was added over a period of 20 min a solution of 1.00 g (2.28 mmol) of **6** in 30 ml of tetrahydrofuran. Refluxing was continued for 18 hr and then 15 ml of commercial anhydrous ether was added slowly followed by dropwise addition of 15 ml of ethyl acetate to destroy any unreacted $LiAlH_4$. The reaction mixture was filtered and the filtrate was evaporated to give 215 mg (47%) of crude *N*-benzyl-*p*-toluidine.

Reduction of 6 by Zinc and Glacial Acetic Acid. To a stirred solution of 452 mg (1.03 mmol) of **6** in 10 ml of dry tetrahydrofuran and 12.5 ml of glacial acetic acid was added in portions over a 5-min period 5.0 g of zinc dust. The mixture was stirred for 4.5 days and filtered. The filtrate was diluted with 25 ml of water and extracted with six 15-ml portions of C_6H_6. Evaporation of the benzene gave 64 mg (31%) of *N*-benzyl-*p*-toluidine.

Pyrolysis of 6. Formation of N-Benzal-p-toluidine. In a vacuum sublimator was placed 300 mg (0.685 mmol) of **6** and the pressure was lowered to not less than 10 mm. The sublimator chamber containing the sample was immersed in an oil bath held at 200°. Compound **6** melted and bubbled vigorously. After 5 min the oil bath was removed, the wall of the sublimator was rinsed with ether, and the washings were saved. The residual black tar in the reaction chamber was extracted with ether and the ether solutions were pooled and evaporated. The *N*-benzal-*p*-toluidine weighed 43 mg (32%) and was identified by comparison of its infrared spectrum with that of an authentic sample.

Isomerization of 1-(p-Nitrobenzoyl)aziridine to 2-(p-Nitrophenyl)-2-oxazoline. A mixture of 384 mg (2.04 mmol) of 1-(*p*-nitrobenzoyl)aziridine and 40 mg (0.29 mmol) of α-phenyl-*N*-methylnitrone and 20 ml of *m*-xylene was refluxed for 4.5 hr. The solvent was evaporated and the residual oil was triturated with a small quantity of ether. Filtration gave 306 mg (80%) of crude 2-(*p*-nitrophenyl)-2-oxazoline which melted after recrystallization from 95% ethanol at 176–182° (lit.[14] mp 180–181°).

In another run 384 mg (2.00 mmol) of 1-(*p*-nitrobenzoyl)aziridine and 270 mg (2.00 mmol) of α-phenyl-*N*-methylnitrone gave a lower yield of oxazoline (29%) probably because of the difficulty of separating the oxazoline from the excess nitrone. It was possible in this experiment to isolate 6.6% of the oxadiazine **13** from the filtrate that was obtained after isolating the 2-*p*-nitrophenyl-2-oxazoline.

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Registry No. **4**, 50259-95-5; **5**, 50259-96-6; **6**, 50546-29-7; **7**, 50259-97-7; **8**, 50259-98-8; **9**, 50259-99-9; **10**, 50260-00-9; **11**, 50260-01-0; **12**, 50431-02-2; **13**, 50260-02-1; **17**, 42790-37-4; *N*-(β-hydroxyethyl)-3,4-dichlorobenzamide, 28298-26-2; 2-methoxy-5-nitro-4′-aminodiphenylmethane, 42790-36-3; *p*-nitrotoluene, 99-99-0; *p*-nitroanisole, 100-17-4; acetonitrile, 75-05-8.

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