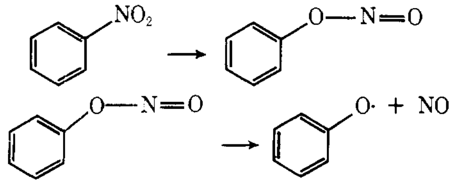
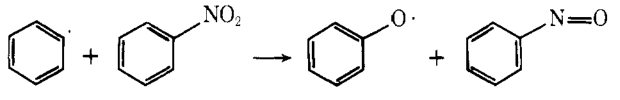
The major difference between this mechanism and that proposed by Fields and Meyerson[8] is that we do not postulate as a primary step the direct fission of nitrobenzene to NO_2 and phenyl radical, a step which, in our view, is not supported by the evidence. Also, in our experiments phenol was not observed as a product of nitrobenzene pyrolysis under any circumstances, whereas Fields and Meyerson reported phenol as the most prominent product at 600 °C. This again supports the conclusion that heterogeneous processes are of great importance in pyrolyses of aromatic nitro compounds. Formation of phenolic products most probably involves the prior production of phenoxy radical, either by



or by



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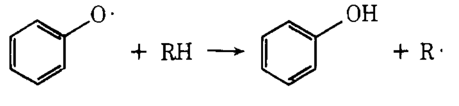

without specifying whether these are homo- or hetereogeneous processes.

As we have stressed, surface reactions play a dominant role in pyrolyses. It might therefore be asked, what is the evidence for a *homogeneous* mechanism. The answer, considering both present and previous results, is that even though many of the reactions discussed above could proceed as uni- or bimolecular gas phase reactions, there is *no* evidence that nitrobenzene pyrolysis takes place to any extent by a homogeneous mechanism.

Registry No.—Nitric oxide, 10102-44-0; nitrobenzene, 98-95-3.

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(10) The NO_2 was stored in a flask equipped with a rubber septum, which after a time was degraded by the NO_2, with the resulting production of CO_2. As described above, our test for NO_2 was not affected by the presence of CO_2, even in relatively large amounts.

Dry Ozonation of Amines. Conversion of Primary Amines to Nitro Compounds

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An efficient synthetic method for the conversion of primary amines into their nitro derivatives is described. The amines, adsorbed on dry silica gel, are ozonized to give mainly the corresponding nitro compounds. The dependence of the product yields on several experimental factors was investigated.

Saturated primary amines undergo oxidation reactions by ozone in solution.[1,3] These reactions, thoroughly investigated by Bailey and his co-workers[1,2] result in the corresponding nitroalkanes accompanied by several other compounds depending on the reaction conditions. The by-products are derived mainly from the partially oxidized amines, which react with the solvent, with the solvent oxidation products, or with each other. In addition, competitive reactions of ozone with C atoms were intermittently observed. Therefore nitroalkanes are formed in modest yields and their isolation necessitates separation from the accompanying by-products limiting the preparative value of ozonation in solution.

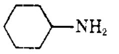
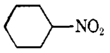
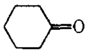
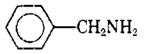
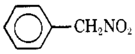
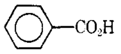
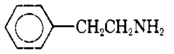
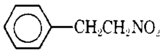
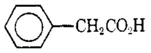
In order to overcome these drawbacks, we have applied our recently described method of ozonation on silica gel.[4] We have used this dry ozonation method to convert primary amines (alkyl, alkyl aryl, and aryl) into the corresponding nitroalkanes.

The oxidation procedure is carried out as follows. The amine is absorbed on the silica gel ca. 100 times its weight, either by mixing the dry materials in a closed flask or by impregnation using volatile solvent. The adsorbed silica gel is then cooled to −78 °C and ozone is passed through it (3 equiv of ozone is needed). After warming to room temperature, the product may be eluted from the silica gel with an appropriate solvent or by direct vacuum distillation.

Ozonation of Alkyl and Alkyl Aryl Amines. Table I lists the primary amines which were ozonized by our method. Elution of the silica gel with either ether or chloroform gave in all cases, as a major product, the corresponding nitroalkanes, whose yields were between 44 and 70%. The only by-product isolated (except for *tert*-butylamine, whose sole product is the *tert*-nitrobutane) was the respective α-carbonyl derivative (Table I) formed in yields between 2 and 6%. No other products were eluted from the silica gel neither with the solvents mentioned above nor with ethyl acetate.

To obtain optimal conditions for the formation of nitroalkanes we have determined the dependence of the yields of the two reaction products as a function of four experimental factors: concentration of the amine in the silica gel, concentration of water absorbed on the silica gel, reaction temperature, and reaction time. In the first three experiments *sec*-

Table I. Product Yields from Dry Ozonation of Aliphatic Primary Amines

Registry no.	Starting material	Nitro derivative	Yield	Carbonyl derivative	Yield
13952-84-6	$CH_3CH_2CH(CH_3)NH_2$	$CH_3CH_2CH(CH_3)NO_2$	70%	$CH_3CH_2COCH_3$	2%
75-64-9	$(CH_3)_3NH_2$	$(CH_3)_3CNO_2$	70%		
109-73-9	$CH_3(CH_2)_3NH_2$	$CH_3(CH_2)_3NO_2$	65%	$CH_3(CH_2)_2CO_2H$	5%
108-91-8			69%		4%
100-46-9			66%		6%
64-04-0			44%		[a]

[a] Not determined.

Table II. Product Distribution as a Function of *sec*-Butylamine Concentration in Silica Gel.[a]

Amine concn, w/w	2-Nitropropane, %	Ethyl methyl ketone, %
0.13	70.2	1.9
0.21	67.8	1.9
0.37	64.3	3.3
0.60	61.3	5.6
1.00	55.0	6.0
1.7	45.0	6.4
2.7	38.7	7.5
5.2	35.4	7.3
10.5	30.0	9.1

[a] Dry silica gel was used and ozonation performed at −78 °C.

Table III. Product Distribution as a Function of Temperature[a]

Temp, °C	2-Nitropropane, %	Ethyl methyl ketone, %
20	26.9	10.1
0	33.6	7.3
−23	44.8	4.6
−45	51.5	4.5
−63	54.0	4.2
−78	55.5	3.7

[a] Samples of *sec*-butylamine (1%) on dry silica gel were used.

Table IV. Product Distribution as a Function of Water Content in Silica Gel[a]

Water, %	2-Nitropropane, %	Ethyl methyl ketone, %
0	70.0	1.9
0.8	63.3	2.1
2.8	30.6	1.8
4.9	17.6	2.1

[a] Ozonation of *sec*-butylamine (0.12%) was performed at −78 °C.

Table V. Product Distribution as a Function of Reaction Time[a]

Reaction time, min	Nitrocyclohexane, %	Cyclohexanone, %
0.25	22.7	1.0
0.5	40.1	1.6
1	53.0	3.0
2	58.8	4.4
5	60.2	4.2
20	64.5	4.4
30	66.4	4.3

[a] Samples of 10 g of dry silica gel containing cyclohexylamine (0.26%) were ozonized at −78 °C, the ozone flow rate being 0.5 mmol/min.

butylamine was used and the two reaction products were 2-nitrobutane and ethyl methyl ketone. In the last experiment cyclohexylamine was used as a substrate, the products being nitrocyclohexane and cyclohexanone.

Table II describes yields as a function of the *sec*-butylamine starting concentration. On increasing concentration the yield of nitrobutane decreases, at first sharply and, after reaching ca. 2%, slowly.

At higher concentration of the amine, new unidentified dark-colored polar products are formed which were eluted from the silica gel with ethyl acetate. These may be derived from intermolecular reactions between the ozonation intermediates and the starting amines, since at concentration above 2%, all the silica grains are already covered with monolayer,[5] by the absorbed material. The yields of nitrobutane decrease with temperature increase (Table III) and with the increase of water content of the silica gel (Table IV).

It appears from Table V that the oxidation rate at −78 °C is fast and the formation of nitrobutane is completed after only 2 min. During this time ca. 3 equiv of ozone (in relation to the starting amine) has passed through the silica, which amounts to the quantity necessary for a complete conversion of the butylamine to 2-nitrobutane. Thus the reaction between ozone and the primary amine is instantaneous, the reaction rate probably being equal to the diffusion rate of ozone into the silica grains.

The ozonation mechanism of amines is probably similar to that proposed by Bailey et al.[1,2] for ozonation in solution. The pathway leading to the formation of nitro derivatives involves an electrophilic attack of ozone on the amine nitrogen, leading to an adduct, which is in an equilibrium with the anion radical. Decomposition of the adduct leads to the amine oxide, the precursor of the nitro derivative.

The fact that the yield of the carbonyl compounds is less dependent on the reaction conditions than the yield of the nitro derivatives points to different pathways for their formation. We assume that a direct attack of ozone on the activated α-carbon hydrogen bond occurs concurrently with that on the amine nitrogen leading to the α-hydroxy amines, whose decomposition generates the carbonyl function (Scheme I). This second pathway was also suggested originally by Bailey[1b,6,7,8] as an alternative mechanism for the formation of carbonyl derivatives on ozonation in solution. Similar insertion of oxygen into C–H bonds was previously observed in other saturated compounds.[4,9,10]

Scheme I

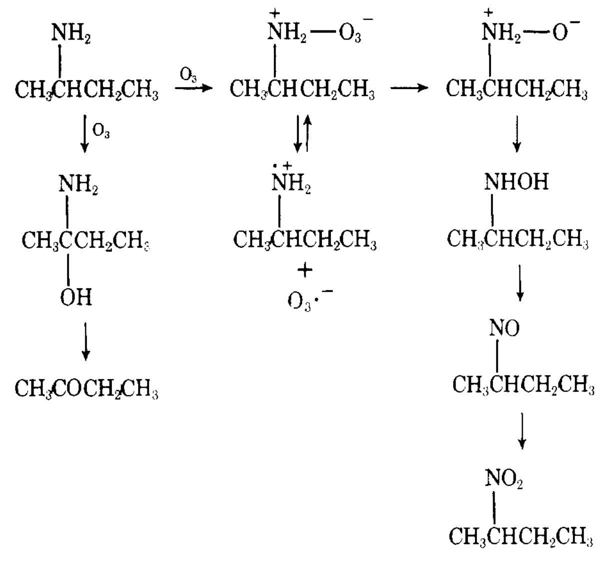
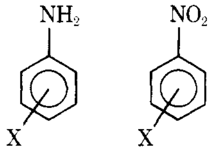


Table VI



Registry no.	X	Yield, %
618-87-1	3,5-di-NO_2	2.8
99-09-2	*m*-NO_2	3.2
100-01-6	*p*-NO_2	5.5
106-49-0	*p*-CH_3	9.6
62-53-3	H	12.5
104-94-9	*p*-OCH_3	13.2
106-47-8	*p*-Cl	20.5
106-40-1	*p*-Br	19.8

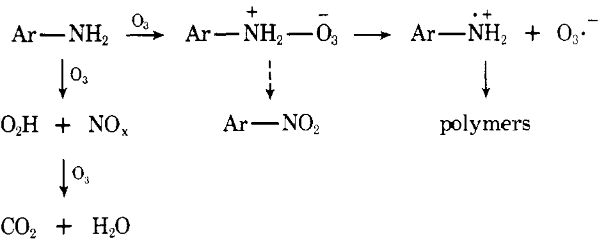
Ozonation of Anilines. Series of anilines were ozonized under similar conditions as for the aliphatic amines (Table VI). Since most of these aromatic amines were solids, the adsorption was done by dissolving the amines in methylene chloride, followed by evaporation on the rotatory evaporator. The products were eluted from the silica gel with methylene chloride. Although the yields of the nitro derivatives were generally low, they were obtained as pure crystalline materials.

Though the yields of the various nitrobenzenes formed from anilines upon peracid oxidations (Emmons reaction)[11,12] are considerably higher than upon ozonation, there is a distinct relationship between yields of the respective nitrobenzenes formed by the two methods. This similarity derives from the fact that both oxidations proceed by electrophilic attack of oxygen atom on the aniline nitrogen atom.

The low yields of the nitrobenzenes may be explained by the reduced nucleophilicity of the NH_2 group and by the competitive oxidation of the benzene ring. Thus substitution with the electron-withdrawing NO_2 group further reduces the NH_2 nucleophilicity while substitution with electron-donating OCH_3 or CH_3 functions increases the nucleophilicity of the benzene ring, both contributing to the low yield of the nitrobenzenes. On the other hand, the substitution by halogens deactivates the amine function less than the aromatic ring resulting in moderate yields of the halogenonitrobenzenes.

The yield of nitrobenzenes depends on the water content of the silica gel and on the reaction temperature (as in the case of alkyl and alkyl aryl amines) but it is independent of the concentration of the starting materials. At higher concentration, although the yield of nitrobenzene remained constant, an increasing amount of nitrogen oxides, carbon dioxide, formic acid, and black polymeric materials (aniline black) were formed. These products are a result of a direct oxidation of the aromatic ring leading to nitrogen oxide and formic acid, which gives upon further oxidation carbon dioxide. It is to be pointed out that the nitrobenzenes themselves under these conditions are generally stable to ozone.

Scheme II



The mechanism for aniline ozonation is depicted in Scheme II. It appears that the ozone–aniline adduct is less stable than the corresponding adduct of alkylamines,[10] decomposing rapidly in two independent pathways. In one, molecular oxygen is evolved resulting in formation of nitrobenzene, and in the other the radical formed from the adduct irreversibly leads to polymeric materials.

The particular advantages of the dry ozonation of amines are the simplicity of the experimental procedure, the ease of product isolation, the purity of the isolated products, and short reaction times. Further application of this method to other functionalized amines, like amino acids and polypeptides, is under investigation.

Experimental Section

General Procedure for Dry Ozonation of Alkyl and Aryl Alkyl Amines. The alkyl and aryl alkyl amines (which are all liquids) were absorbed on the silica gel by thorough mixing with dry silica gel (Merck, Kieselgel 60, 70–230 mesh, dried for 24 h at 450 °C). The silica gel (ca. 30 g) containing the adsorbed material (0.1–0.2% w/w) was cooled to −78 °C and a stream of 3% ozone (in oxygen) (generated from a Welsbach ozonizer) passed through it.

The silica gel was allowed to warm to room temperature, and the material was eluted with an organic solvent. All the products were identified with authentic samples by means of NMR, GC, and IR spectra. The quantitative estimations were done by integration of the GC peaks in relation to reference substances using a 3 m × 0.125 in. column of 20% Carbowax 20M on Chromosorb W as follows.

***sec*-Butylamine.** Elution was done with anisole which was directly injected into the GC, at 109 °C together with 1-nitropropane serving as internal standard. Two products, 2-nitrobutane (70%) and ethyl methyl ketone (2%), were identified. ***tert*-Butylamine.** The products were eluted with diethyl ether and the solution containing 1-nitropropane as internal standard was injected into GC (107 °C). 2-Methyl-2-nitropropane (70% yield) was the only detected product. ***n*-Butylamine.** Elution with diethyl ether. The reference material was diethyl malonate (160 °C); the main product was 1-nitrobutane (65%) accompanied by 5% butyric acid. **Cyclohexylamine.** Elution as above. Diethyl malonate was used as internal standard (163 °C). The main product was nitrocyclohexane (69%) accompanied by cyclohexanone (4%). **β-Phenylethylamine.** Elution of the product was done by chloroform. The product, 2-phenyl-1-nitroethane (44% yield), was pure and no other products were eluted from the silica gel. **Benzylamine.** Elution of the product was done with chloroform. The main product was α-nitrotoluene (66%) accompanied by 6% of benzoic acid.

General Procedure for Dry Ozonation of Anilines. The anilines were impregnated on dry silica gel by dissolving them in methylene chloride, adding the silica gel, and evaporation of the solvent, using a rotatory evaporator, their concentration in the silica gel being 0.15–0.20%. Ozonation was done as described above. Elution of the products was done with methylene chloride, which was evaporated to dryness, resulting in crystalline nitrobenzenes in high degree of purity, as shown by their NMR and UV spectra. Quantitative estimations were done by measuring the optical density of their methanolic solutions; yields are given in Table VI.

Product Distribution as a Function of the Aniline Concentration. The experiment was performed with aniline and *p*-nitroaniline, the concentration range being between 0.1 and 13% w/w. The yields of nitrobenzene and *p*-dinitrobenzene were 12.5 ± 0.5 and 5.5 ± 0.5%, respectively, in all concentrations. At concentrations above 0.5, increasing amounts of dark viscous polymers and formic acid were eluted with a mixture of methanol–ethyl acetate (1:1). Water extract of the silica gel gave positive test for nitrate ions (precipitation in the presence of nitron solution[13]).

Ozonation of Formic Acid. Silica gel, adsorbed with pure formic acid (1%), was saturated with ozone at −78 °C. The outlet gas was allowed to bubble through a aqueous barium hydroxide solution. A white precipitate of barium carbonate indicated the formation of carbon dioxide. After 0.5 h 47% of formic acid was regenerated by ether extraction of the silica gel.

Registry No.—Anisole, 100-66-3; 1-nitropropane, 108-03-2.

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Study on the Adduct of Ketenimine and Aziridine

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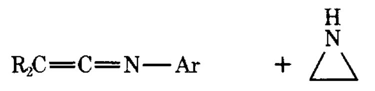
The reaction of *N*-arylketenimines **1a–c** with aziridine gave the imidoylaziridines **3a–c** in excellent yields. However. *N*-cyclohexylketenimine **1d** gave the rearranged product, the imidazoline **5d.** Syn–anti isomerism of the imidoylaziridines was found by NMR spectroscopy. Acidic treatment of **3a,b** in ethanol resulted in ring expansion to the imidazolines **5a,b** or addition of the solvent to the aziridine ring according to acids. Diphenylketene cycloadded to the C=N bond of the imidoylaziridine **3a**, while no reaction with phenyl isocyanate and phenyl isothiocyanate was observed.

For preparative purposes the addition of aziridine to heterocumulenes followed by ring expansion seems to provide a convenient method.[1] This reaction seems not to have been studied. In the present paper we report the addition of ketenimines with aziridine and some chemical properties of the adducts, imidoylaziridines.[2] We also discuss syn–anti isomerism of the imidoylaziridines by NMR spectroscopy.

Preparation and Syn–Anti Isomerism. The reactions of *N*-arylketenimines **1a–c** with aziridine (**2**) gave imidoylaziridines **3a–c** quantitatively at room temperature. On the other hand, preparation of **3a** from *N*-phenylisobutyrimidoyl chloride and aziridine was not successful because of ring expansion of the expected aziridine during workup. Therefore the reaction of ketenimines is superior to the other method with respect to avoiding contaminants and handling with unstable aziridines. The isolated products consisted of syn and anti isomers.



1a, R = Me; Ar = Ph
b, R = Ar = Ph
c, R = Ph; Ar = *p*-$CH_3C_6H_4$

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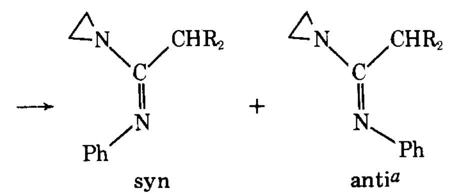
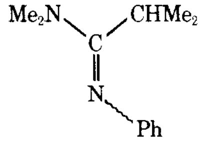


	syn	anti[a]
3a	52%	48%
3b	68	32
3c	73	27

[a] Determined by NMR at 23 °C in $CDCl_3$.

The NMR spectrum of **3a** (at 23 °C) had two singlets at δ 1.82 and 2.15, which were assigned to the protons of the aziridine ring. The methyl protons exhibited two doublets at δ 1.15 and 1.27. At 100 °C, the signals of aziridinyl and methyl protons converted into one singlet at δ 1.94 and one doublet at δ 1.18 (in Me_2SO-d_6), respectively. These signals returned to the original pattern by lowering the temperature. Though aziridinyl protons are often observed as multiplets, rapid inversion of the aziridine ring caused the four ring protons to become equivalent in this case. The signal of aziridinyl protons of the syn isomer appeared in lower field than that of the anti isomer because of the shielding effect of the phenyl group lying close to the aziridine ring. In comparison with the adduct **4** from dimethylamine and the ketenimine **1a,** whose NMR spectrum showed only one set of isopropyl and *N*-methyl signals at 23 °C,[3] syn–anti isomerization of **3a** was slower than that of **4**. The rate of the isomerization seemed to depend on the electron-donating ability of the amino group to the C=N bond.



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