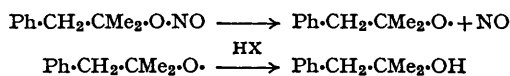**1097.** *Aryl-substituted Tertiary Alkoxyl Radicals. Part II.[1]*
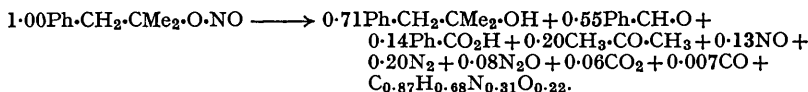*Thermal Decomposition of αα-Dimethylphenethyl Nitrite.*

By Peter Gray and M. J. Pearson.

As the last of a series of investigations of aryl-substituted alkyl nitrites, the thermal decomposition of αα-dimethylphenethyl nitrite has been investigated. Decomposition has been carried out over the range 130—170° in the pure liquid and in solution. The first step is O–N bond fission. In cumene solution, a hydrogen donor, fission is succeeded by hydrogen abstraction, and yields of alcohol approaching 100% conversion are found:

$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot NO \longrightarrow Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot + NO$$

$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot \xrightarrow{HX} Ph \cdot CH_2 \cdot CMe_2 \cdot OH$$

---

[1] Part I, P. Gray and M. J. Pearson, preceding Paper.

View Online

[1964] *Aryl-substituted Tertiary Alkoxyl Radicals. Part II.* 5735

The principal products of decomposition of the pure liquid are 1,1-dimethyl-2-phenylethanol, benzaldehyde, acetone, and benzoic acid. There is considerable reduction to nitrogen and nitrous oxide of the nitric oxide initially formed. At 150°, decomposition may be represented by the overall equation:

$$1 \cdot 00 Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot NO \longrightarrow 0 \cdot 71 Ph \cdot CH_2 \cdot CMe_2 \cdot OH + 0 \cdot 55 Ph \cdot CH \cdot O +$$
$$0 \cdot 14 Ph \cdot CO_2 H + 0 \cdot 20 CH_3 \cdot CO \cdot CH_3 + 0 \cdot 13 NO +$$
$$0 \cdot 20 N_2 + 0 \cdot 08 N_2 O + 0 \cdot 06 CO_2 + 0 \cdot 007 CO +$$
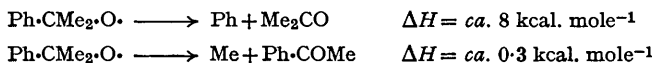$$C_{0 \cdot 87} H_{0 \cdot 68} N_{0 \cdot 31} O_{0 \cdot 22}.$$

Decomposition is autocatalytic, following first-order kinetics only in the initial stages. Artificially added benzaldehyde greatly increases the rate; and its formation is thought to be the origin of the autocatalysis, as is the case for benzyl nitrite pyrolysis.
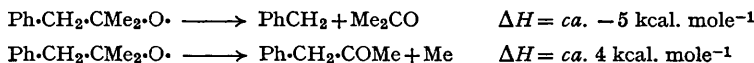
The free αα-dimethylphenethyloxy-radical undergoes some decomposition. As is to be expected on thermochemical grounds, this is by loss of a benzyl radical, leaving acetone: there is no evidence for methyl-radical loss or for benzylacetone formation.

The two tertiary aryl-substituted radicals, αα-dimethylbenzyloxyl (studied in Part I) and αα-dimethylphenethyloxyl thus show some differences from the closely related primary and secondary radicals (benzyloxyl and α-methylbenzyloxyl) studied earlier. The Paper ends with a brief comparison of the family relationships.

A BRIEF account of the general mechanism for the thermal decomposition of alkyl nitrites was given in the preceding Paper[1] on αα-dimethylbenzyl nitrite. Special reference was made there to tertiary nitrites since αα-dimethylbenzyl nitrite was the first aryl-substituted tertiary alkyl nitrite to be investigated. The results obtained indicated that when unimolecular decomposition of the αα-dimethylbenzyloxyl radical occurred it proceeded exclusively by elimination of the methyl radical, no evidence being found for the formation of free phenyl radicals. This result is in accord with the thermochemical requirements for the alternative modes of decomposition, as indicated below:
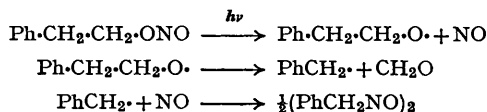
$$Ph \cdot CMe_2 \cdot O \cdot \longrightarrow Ph + Me_2 CO \qquad \Delta H = ca. \ 8 \ kcal. \ mole^{-1}$$
$$Ph \cdot CMe_2 \cdot O \cdot \longrightarrow Me + Ph \cdot COMe \qquad \Delta H = ca. \ 0 \cdot 3 \ kcal. \ mole^{-1}$$

However, in the related alkoxyl radical ($Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot$), in which the phenyl group is replaced by a benzyl group, the thermochemical situation is changed. Unimolecular elimination of the methyl radical may now not occur since it is thermochemically less favourable than elimination of the benzyl radical:

$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot \longrightarrow PhCH_2 + Me_2 CO \qquad \Delta H = ca. \ -5 \ kcal. \ mole^{-1}$$
$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot \longrightarrow Ph \cdot CH_2 \cdot COMe + Me \qquad \Delta H = ca. \ 4 \ kcal. \ mole^{-1}$$

The αα-dimethylphenethyloxyl radical might also be expected to show a lower overall stability than αα-dimethylbenzyloxyl, as shown, *e.g.*, when the relative extents of alcohol formation by hydrogen abstraction and ketone formation by bond fission are compared.

A somewhat similar situation exists in the photolysis of the aryl-substituted primary alkyl nitrites $Ph \cdot [CH_2]_n \cdot O \cdot NO$, a process which yields nitric oxide and the alkoxyl radical as the initial step. It has been found[2] that when $n = 1$ or 3 (*i.e.*, in benzyl nitrite and 3-phenylpropyl nitrite), the nitroso-compounds which would have been indicative of the formation of free phenyl or phenethyl radicals, respectively, are absent. On the other hand, when $n = 2$ (phenethyl nitrite) there is a high yield (43%) of nitrosotoluene as a result of the lower stability of the benzyl–carbon bond in the phenethyloxyl radical:

$$Ph \cdot CH_2 \cdot CH_2 \cdot ONO \xrightarrow{h\nu} Ph \cdot CH_2 \cdot CH_2 \cdot O \cdot + NO$$
$$Ph \cdot CH_2 \cdot CH_2 \cdot O \cdot \longrightarrow PhCH_2 \cdot + CH_2 O$$
$$PhCH_2 \cdot + NO \longrightarrow \tfrac{1}{2}(PhCH_2 NO)_2$$

[2] P. Kabasakalian, E. R. Townley, and H. D. Yudis, *J. Amer. Chem. Soc.*, 1962, **84**, 2716.

Both to test these expectations and to glean more information about the behaviour of aryl-substituted tertiary alkyl nitrites, the thermal decomposition of αα-dimethylphenethyl nitrite has been investigated. Establishing the nature of the initial step and the stoicheiometry of the decomposition, and assessing the importance of alkoxyl radicals in this system are among the other aims of this work.

<h1 style="text-align:center">EXPERIMENTAL</h1>

Materials.—αα-Dimethylphenethyl nitrite was prepared [3] by the action of aqueous sodium nitrite and aqueous aluminium sulphate on cold 1,1-dimethyl-2-phenylethanol. The crude nitrite was purified by washing, drying, and fractionation *in vacuo*. It was stored *in vacuo* at −196° in the dark.

1,1-Dimethyl-2-phenylethanol, cumene, and benzaldehyde were purchased from B.D.H., Ltd. The benzaldehyde was purified by fractionation *in vacuo* immediately prior to use, in order to remove traces of benzoic acid. Oxygen-free nitrogen was obtained from British Oxygen Co. Ltd.

Spectra.—There are no previous records of either the infrared or ultraviolet spectra of αα-dimethylphenethyl nitrite, and these spectra are therefore given below.

The infrared spectrum was determined from a thin film of the liquid nitrite in a Grubb–Parsons double-beam recording spectrometer; absorption maxima were observed at the following wavelengths (μ): 3·32w, 3·37m, 3·42w, 6·11vs, 6·67w, 6·87w, 7·20w, 7·29m, 7·93vw, 8·16w, 8·43vw, 8·80w, 8·91w, 9·71vw, 10·57vw, 12·12s, 12·57s, 12·95vs, 13·56s, 14·25s.

Ultraviolet spectra of solutions in light petroleum were recorded on an Optica double-beam absorption spectrometer. Locations of absorption maxima in mμ (and corresponding extinction coefficients) are: 328 (5), 337·5 (27), 353·5 (57), 367 (71), 383 (80), 398·5 (64). Both these spectra show the same characteristics of a *trans*-nitrite as did the spectra of αα-dimethylbenzyl nitrite, thereby adding to the number of tertiary nitrites known [4] to exist preferentially in the *trans*-form.

Procedure.—Decompositions were carried out under nitrogen in the pure liquid state and in solution in an apparatus similar to that [5] described previously. The gaseous and the liquid products were characterized and analysed quantitatively. The progress of the decomposition was followed by measurement of the evolved gases by means of a constant-pressure gas burette.

Analysis of the Liquid Products.—The liquid product of the decomposition contained 1,1-dimethyl-2-phenylethanol, benzaldehyde, acetone, and a little benzoic acid and water. The products were identified by vapour-phase chromatography employing three different types of column at temperatures ranging from 40° to 200°. The peak that corresponded to 1,1-dimethyl-2-phenylethanol was always by far the largest. A polyethylene glycol column gave the best separation of the products; it indicated, in addition to the large amount of the alcohol, smaller quantities of benzaldehyde and acetone, and traces of the olefin, 2-benzylpropene. The chromatogram showed no evidence for the presence of either bibenzyl or benzylacetone. Infrared spectra of the decomposition products as thin films supported the gas-chromatographic analysis, a large OH peak at 2·90 μ confirming large quantities of the alcohol and a broad peak for the C=O stretching frequency (5·80—5·90 μ) indicating the presence of several carbonyl compounds. (Carbonyl absorption of standard samples were: benzaldehyde 5·87 μ, benzoic acid 5·82 μ, acetone 5·81 μ.)

The identity of 1,1-dimethyl-2-phenylethanol was further confirmed by its boiling point. It was estimated quantitatively by infrared spectroscopy against standard solutions in chlorobenzene from the 2·90 μ peak. The benzaldehyde and acetone were estimated by gas chromatography using the 1,1-dimethyl-2-phenylethanol peak as a known standard and calibrating the peaks with standard solutions of the three components in similar ratios to those found in the products. Benzoic acid was determined as in earlier [1,5,6] decompositions and these estimations agreed with those from peak areas on the gas chromatograms.

Analysis of Gaseous Products.—The gaseous products of the decomposition contained nitric oxide, nitrous oxide, nitrogen, carbon dioxide, and some acetone. Except for the last, these had all been found as products of the decomposition of αα-dimethylbenzyl nitrite [1] and were

[3] A. Chrétien and Y. Longi, *Compt. rend.*, 1945, **220**, 746.
[4] P. Gray and M. J. Pearson, *Trans. Faraday Soc.*, 1963, **59**, 347.
[5] P. Gray, P. Rathbone, and A. Williams, *J.*, 1960, 3932.
[6] P. Gray, M. J. Pearson, and P. Rathbone, *J.*, 1961, 4006.

View Online

[1964]   *Aryl-substituted Tertiary Alkoxyl Radicals. Part II.*   5737

accordingly determined qualitatively and quantitatively in an identical manner. The acetone was estimated from its carbonyl stretching frequency (*ca.* 5·8 μ) in the infrared spectrum of the gaseous products.

RESULTS

Decomposition of Pure Liquid αα-Dimethylphenethyl Nitrite.—When a sample of the nitrite was exposed to the atmosphere at room temperature, decomposition took place gradually over several days. The liquid product was pale yellow and was almost entirely 1,1-dimethyl-2-phenylethanol; therefore, decomposition in air was probably occurring almost exclusively by hydrolysis, unlike those of benzyl[4] and α-methylbenzyl[5] nitrites.

Stoicheiometry.—The pure liquid nitrite was decomposed under an inert (nitrogen) atmosphere at temperatures from 132° to 169°. At the lower end of the temperature range, decomposition took about 36 hr. to complete; the majority of decompositions were therefore conducted at higher temperatures. At 151° and 169°, decomposition took about 8 and 3 hr., respectively. As the decomposition proceeded, the initial pale yellow colour of the nitrite gradually changed to a deep-red-brown. The products of the decomposition were 1,1-dimethyl-2-phenylethanol, benzaldehyde, acetone, benzoic acid, nitric oxide, nitrous oxide, nitrogen, and carbon dioxide. Neither benzylacetone nor bibenzyl was found.

The yields of the major products of decomposition of the pure liquid nitrite at 132°, 151°, and 169° are given in Table 1. 1,1-Dimethyl-2-phenylethanol was the principal product in the liquid phase at all temperatures. Nitrogen and nitrous oxide were the major gaseous products,
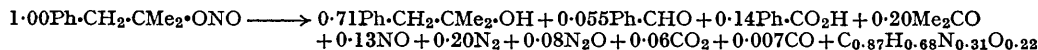
TABLE 1.

Product analysis for the decomposition of liquid αα-dimethylphenethyl nitrite and the influence on the stoicheiometry of added benzaldehyde (products are expressed as moles/100 moles nitrite).

Run no.	Decomp. temp.	Decomp. time (hr.)	Ph·CH$_2$·CMe$_2$·OH	Me$_2$CO*	Ph·CHO	Ph·CO$_2$H	NO	N$_2$O	CO$_2$	N$_2$	Gas total
3	132°	36½	74		3·0	12·9	14·0	6·5	1·8	20	51
4	132	61	74	11	3·8	12·1	14·5	9·0	6·0	21	57
1	151	6¾	71		4·7	14·0	12·3	6·4	3·2		51
5	151	14½	71	20	5·7	13·7	13·3	8·3	6·8	19	49
6	151	9	71	19	5·7	13·8	13·3	7·1	4·0	20	53
9	151	10½			5·3					21	52
8	151	4¼					5·7	2·2	0·2	11·3	23
2	169	2¾	68	29	8·7	15·7	12·5	7·3	1·4	25	51
7	169	4½	69	25	8·1	14·9	12·9	6·4	2·3	24	51
10	169	4¾	67	27	8·9	15·2	13·5	5·7	1·1	23	51
			αα-Dimethylphenethyl nitrite in the presence of added benzaldehyde (molar ratio 1:1)								
15	151	½				34	3·8	24·2	2·9	14·5	
13	151	2¼				36	4·4	23·9	2·7	15	44

* Experimental difficulties hindered accurate determination.
In addition to the above products, the following minor products were obtained: H$_2$O ∼ 4 mole, CO ∼ 0·7 mole.

their yields not varying much with the extent of decomposition. The nitric oxide yield was noticeably small compared to the value that is theoretically possible. Nitrous oxide, although by no means a major product, was formed in greater yield than is normally observed in nitrite pyrolyses, the percentage increasing slightly as the reaction proceeded. Carbon dioxide appeared to be formed principally in the final stages of the decomposition. The overall stoicheiometry at 151° may be represented by the overall equation:

$$1·00 \text{Ph·CH}_2\text{·CMe}_2\text{·ONO} \longrightarrow 0·71 \text{Ph·CH}_2\text{·CMe}_2\text{·OH} + 0·055 \text{Ph·CHO} + 0·14 \text{Ph·CO}_2\text{H} + 0·20 \text{Me}_2\text{CO}$$
$$+ 0·13 \text{NO} + 0·20 \text{N}_2 + 0·08 \text{N}_2\text{O} + 0·06 \text{CO}_2 + 0·007 \text{CO} + \text{C}_{0·87}\text{H}_{0·68}\text{N}_{0·31}\text{O}_{0·22}$$

Only 69% of the total nitrogen from the original nitrite grouping was to be found among the gaseous products. Microanalysis showed that the liquid products contained 2·05% of nitrogen, corresponding to 0·27 atom of nitrogen per mole of initial nitrite; 96% of the nitrogen was thus accounted for in the two phases.

Change of temperature had only a small effect upon the product composition. The acetone,

benzaldehyde, and benzoic acid yields all increased slightly at the higher temperatures, but the remaining products were relatively unaffected by temperature. Approximately 90% of the phenyl groups were accounted for, as 1,1-dimethyl-2-phenylethanol, benzaldehyde, and benzoic acid, and the analyses can therefore be said to be reasonably complete.

Kinetics.—The progress of the decomposition of αα-dimethylphenethyl nitrite was followed by measuring the volume of gas evolved as a function of time. These results are shown in Fig. 1
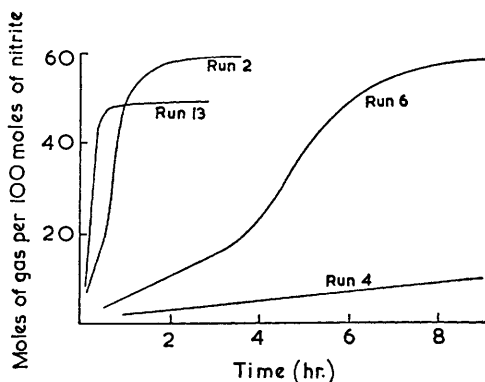
FIG. 1. Gas evolution during decomposition of liquid αα-dimethylphenethyl nitrite (results for 4 selected runs); runs 2, 4, 6, pure nitrite at 132°, 151°, and 169°, respectively; run 13, nitrite plus initially added benzaldehyde (molar ratio 1:1) at 151°.
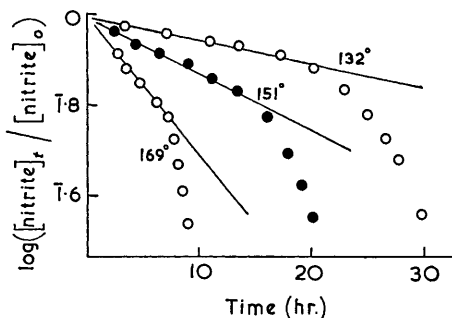
FIG. 2. First-order plots ($1 + \log[\text{nitrite}]_t/[\text{nitrite}]_0$ against time) for thermal decomposition of αα-dimethylphenethyl nitrite at 132°, 151°, and 169°, showing onset of departure from first-order kinetics.

as a graph of the moles of gas produced (per 100 moles of nitrite) against elapsed time for decomposition at 132° (run 4), 151° (run 6), and 169° (run 2). It is noteworthy that decomposition exhibited autocatalysis throughout the temperature range although the effect was most marked at the lower temperatures. At 132°, only 25% decomposition had taken place after 21 hr., yet decomposition was half over after about 26 hr. and virtually complete after 38 hr. Half-lives at 151° and 169° were *ca.* 4·5 hr. and 0·8 hr.

The concentration of nitrite remaining in the decomposition mixture at a certain time can be deduced by assuming that the rate of gas evolution is a roughly constant function of the rate of decomposition of the nitrite. This assumption was made for α-methylbenzyl[5] and αα-dimethylbenzyl[1] nitrites and is unlikely to lead to gross error. It is supported by the relative constancy of product compositions found here.

The graphs corresponding to first-order decomposition were constructed by plotting $\log\{[\text{nitrite}]_t/[\text{nitrite}]_0\}$ against time (see Fig. 2 for runs at 132°, 151°, and 169°). The plot was linear for nearly 35% of the decomposition, then it began to deviate rather sharply from the straight line in the direction of accelerated reaction. Values of the first-order rate constant evaluated from the straight line portion of these plots were:

Temp. (°C)	132	151	169
10^5k (sec.$^{-1}$)	0·32	1·39	20·8

An Arrhenius plot of the above values gave an activation energy of 40 kcal. mole^{-1} and a pre-exponential factor of 10^{16} sec.$^{-1}$. Bearing in mind the limitations of this treatment we see that these values are similar to those obtained[1] for αα-dimethylbenzyl nitrite.

Decomposition of αα-Dimethylphenethyl Nitrite in Cumene Solution.—To establish whether the αα-dimethylphenethyloxyl radical was formed in the initial step of the decomposition, a few runs were conducted in the presence of an efficient hydrogen-atom source, cumene. Solutions of the nitrite in cumene (0·04—0·15M) were decomposed to completion at 151°. Decomposition was much faster than for the pure nitrite. The yield of 1,1-dimethyl-2-phenylethanol was found to increase as the nitrite concentration decreased, so that yields approaching 100% conversion of the nitrite into the alcohol were obtained when the initial nitrite concentration was reduced to 0·04 mole l.$^{-1}$.

[1964] *Aryl-substituted Tertiary Alkoxyl Radicals. Part II.* 5739

View Online

Decomposition in the Presence of Initially Added Benzaldehyde.—Benzaldehyde has here been established as a decomposition product of pure αα-dimethylphenethyl nitrite. It is also known that benzaldehyde acts as catalyst towards the decompositions of benzyl[5] and α-methylbenzyl[6] nitrites and that it is a product of the former decomposition. Accordingly, mixtures of benzaldehyde with αα-dimethylphenethyl nitrite (molar ratio 1:1) were made up and decomposed at 151° in order to determine whether the benzaldehyde produced was playing an active role in the decomposition. The gas evolution was measured as a function of time and the result is depicted graphically in Fig. 1. The decomposition was accelerated to a rate more than ten times faster than the decomposition of the pure nitrite at the same temperature.

The product yields for the catalysed decompositions are presented in Table 1. They showed changes from those for the pure nitrite. The most noticeable of these was the increased yield of nitrous oxide, this now accounting for nearly 50% of the initial nitrogen. To counterbalance this increase, the yields of nitric oxide and nitrogen decreased and there was slightly less nitrogen present in the liquid phase. The benzoic acid yield showed a 2·5-fold increase.

DISCUSSION

The Initial Step.—There are two clear indications of the nature of the initiating reaction in the thermal decomposition of αα-dimethylphenethyl nitrite: first, the increased yields of 1,1-dimethyl-2-phenylethanol for the runs carried out in the presence of the H-donor solvent, cumene, and second, the high percentage retention of the αα-dimethylphenethyloxyl skeleton in the decomposition products. The initial step must be the fission of the oxygen–nitrogen bond to give the αα-dimethylphenethyloxyl radical and nitric oxide:

$$\text{Ph·CH}_2\text{·CMe}_2\text{·O·NO} \longrightarrow \text{Ph·CH}_2\text{·CMe}_2\text{·O·} + \text{NO} \qquad (1)$$

In this respect it behaves similarly to other alkyl nitrites[7] and in particular to the related tertiary nitrite, αα-dimethylbenzyl nitrite.

Kinetic Aspects and the Origin of Autocatalysis.—Although O–N bond fission is the initial step in decomposition, it cannot be rate-controlling, for the velocity of decomposition is enhanced by H-donors and in their absence, reaction is markedly autocatalytic. The explanation may be expressed in terms of cage effects. A tertiary nitrite, lacking very readily abstractable hydrogen atoms, is a relatively unreactive solvent cage to the initial fission fragments: recombination occurs and the net rate of reaction is thus depressed. A solvent such as cumene, which is readily attacked by the alkoxyl radicals, decreases the proportion of recombination and thus enhances the rate.

Autocatalysis.—The experimental runs conducted in the presence of initially added benzaldehyde demonstrated the large catalytic effect which benzaldehyde has upon the decomposition. It is interesting and revealing to compare these results with those for benzyl nitrite[5] where benzaldehyde is also a product of the decomposition and the kinetics are similar. The effect of initially added benzaldehyde is practically identical in the two systems, similar percentage changes in product yields (Ph·CO$_2$H, NO, N$_2$O, N$_2$) being experienced. It would seem that benzaldehyde is the source of the autocatalysis observed in the decomposition of αα-dimethylphenethyl nitrite, just as it was in benzyl nitrite.

The origin of the autocatalysis lies in the fact that free radicals (alkoxyl radicals) abstract the weakly bound aldehydic hydrogen leaving a free benzoyl radical. Benzaldehyde provides a much more ready source of hydrogen atoms than any other species present in the decomposition and hence formation of 1,1-dimethyl-2-phenylethanol is enhanced and reversal of the initial step diminished. The rate of decomposition is accordingly increased. Other possible rôles for benzaldehyde have been discussed[5,6] previously.

There is a further reaction which may contribute, in part, to the observed autocatalysis, *viz.*, induced decomposition of the nitrite brought about by a benzyl radical abstracting nitric oxide from the parent nitrite:
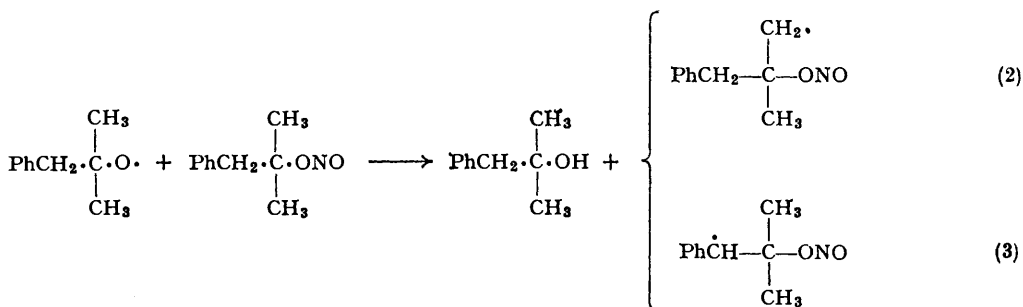
$$\text{Ph·CH}_2\text{·CMe}_2\text{·O·NO} + \text{PhCH}_2\text{·} \longrightarrow \text{Ph·CH}_2\text{·CMe}_2\text{·O·} + \text{Ph·CH}_2\text{·NO}.$$

---

[7] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold, New York, 2nd edn., 1954.

This reaction is not impossible, as parallel reactions have been observed[8] in several other nitrite systems. To the extent that $Ph \cdot CH_2 \cdot CMe_2 \cdot O\cdot$ may furnish fresh $Ph \cdot CH_2\cdot$, short chains are possible.

Stoicheiometry and Origin of the Major Products.—The formation of the products of decomposition has to be explained in terms of the reactions of the $\alpha\alpha$-dimethylphenethyloxyl radical and the nitric oxide molecule. Probable origins for each of the principal reaction products will be discussed in turn. The guiding features are that most of the carbon ends as 1,1-dimethyl-2-phenylethanol, benzoic acid, benzaldehyde, and carbon dioxide; and that the larger part of the nitrogen is accounted for as nitric oxide, nitrous oxide, and nitrogen.

(*a*) 1,1-Dimethyl-2-phenylethanol must originate from the $\alpha\alpha$-dimethylphenethyloxyl radical by H-atom abstraction from some suitable substrate. There are several possible substrates. The first is the most abundant one, *viz.*, the $\alpha\alpha$-dimethylphenethyl skeleton, either in the form of the alkoxyl radical or the parent nitrite. In this skeleton there are primary and secondary hydrogens available for abstraction [reactions (2) and (3)]:

$$PhCH_2 \cdot \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \cdot O\cdot \;+\; PhCH_2 \cdot \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \cdot ONO \longrightarrow PhCH_2 \cdot \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \cdot OH \;+$$

$$PhCH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_2\cdot}{|}}{C}} - ONO \qquad (2)$$

$$Ph\overset{\cdot}{C}H - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - ONO \qquad (3)$$
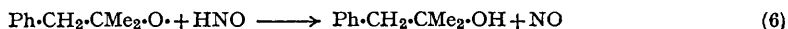
The abstraction of primary hydrogen from a methyl group is not often thermochemically favourable, and the alternative direct abstraction of the secondary H-atoms by the bulky, $\alpha\alpha$-dimethylphenethyloxyl radical will be subject to severe steric hindrance. Therefore, reactions (2) and (3) probably only contribute to a minor extent.
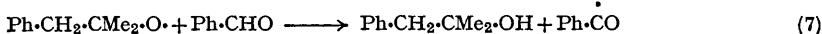
It is more likely that nitric oxide acts as a H-transfer agent. Nitroxyl is known[5, 6, 9] to be an intermediate in nitrite decompositions, being formed when nitric oxide abstracts a H-atom. There is no longer the same severe steric hindrance when nitric oxide removes a secondary H-atom from the $\alpha\alpha$-dimethylphenethyl skeleton [reaction (5)]. Furthermore, Laidler and his co-workers have shown[10] that nitric oxide will abstract primary H-atoms from dimethyl ether:

$$CH_3 \cdot O \cdot CH_3 + NO \longrightarrow \cdot CH_2 \cdot OCH_3 + HNO \qquad (4)$$
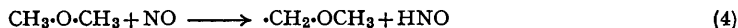
so that nitric oxide may also abstract primary H-atoms from the $\alpha\alpha$-dimethylphenethyloxyl skeleton:

$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot (NO) + NO \longrightarrow Ph \cdot CH \cdot CMe_2 \cdot O \cdot NO + HNO \qquad (5)$$

$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot + HNO \longrightarrow Ph \cdot CH_2 \cdot CMe_2 \cdot OH + NO \qquad (6)$$

The nitroxyl radical has already been established[9] as a donor of H-atoms. Another source of H-atoms is benzaldehyde [reaction (7)]. The aldehydic hydrogen atom is easily abstracted, and so benzaldehyde should provide a (rather small) source of available H-atoms:

$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot + Ph \cdot CHO \longrightarrow Ph \cdot CH_2 \cdot CMe_2 \cdot OH + Ph \cdot \overset{\cdot}{C}O \qquad (7)$$

Abstraction of H-atoms to give 1,1-dimethyl-2-phenylethanol probably takes place concurrently from all these different substrates.

⁸ L. Phillips, *J.*, 1961, 3082; P. Gray and P. Rathbone, *Proc. Chem. Soc.*, 1961, 316.
⁹ J. B. Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.
¹⁰ D. J. McKenney, B. W. Wojciechowski, and K. J. Laidler, *Canad. J. Chem.*, 1963, **41**, 1993.
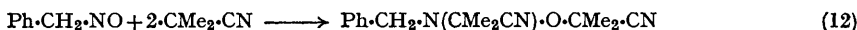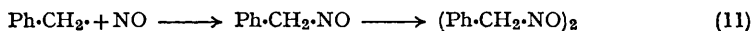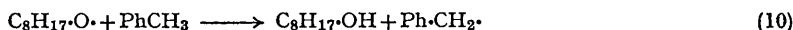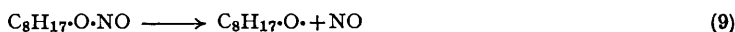
It is noteworthy that 1,1-dimethyl-2-phenylethanol is stable to dehydration under the conditions of decomposition. This is in contrast to $\alpha\alpha$-dimethylbenzyl alcohol which, in the decomposition of $\alpha\alpha$-dimethylbenzyl nitrite, gave[1] large quantities of the corresponding olefin and water.

(*b*) Acetone is formed by the fission of the $\alpha\alpha$-dimethylphenethyloxyl radical [reaction (8)].

$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot \longrightarrow Ph \cdot CH_2 \cdot + Me_2CO \tag{8}$$
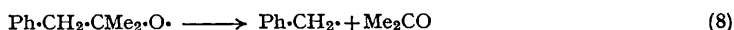
Rupture occurs exclusively at the carbon–benzyl bond, because the products were devoid of any benzylacetone. Therefore, the yield of acetone is a measure of the amount of fission of the alkoxyl radical that is occurring, as opposed to hydrogen abstraction. The reactions of the benzyl radicals are discussed below.

(*c*) Benzaldehyde arises from the oxidation of the benzyl radical formed in reaction (8). Oxidation must be brought about by nitric or nitrous oxides, but from the evidence available it is not possible to postulate a unique mechanism and determine which of the nitrogen oxides is the oxidising agent. It is, however, relevant to consider a system where benzyl radicals are also formed in the presence of nitric oxide. Gingras and Waters[11] decomposed octyl nitrite in toluene solution, firstly in the presence of $\alpha\alpha'$-azoisobutyronitrile and secondly without it. Their findings can be summarized by reactions (9)—(12):

$$C_8H_{17} \cdot O \cdot NO \longrightarrow C_8H_{17} \cdot O \cdot + NO \tag{9}$$

$$C_8H_{17} \cdot O \cdot + PhCH_3 \longrightarrow C_8H_{17} \cdot OH + Ph \cdot CH_2 \cdot \tag{10}$$

$$Ph \cdot CH_2 \cdot + NO \longrightarrow Ph \cdot CH_2 \cdot NO \longrightarrow (Ph \cdot CH_2 \cdot NO)_2 \tag{11}$$

$$Ph \cdot CH_2 \cdot NO + 2 \cdot CMe_2 \cdot CN \longrightarrow Ph \cdot CH_2 \cdot N(CMe_2CN) \cdot O \cdot CMe_2 \cdot CN \tag{12}$$

Neither bibenzyl nor $\alpha\alpha'$-dimethylphenethyl cyanide ($Ph \cdot CH_2 \cdot CMe_2 \cdot CN$) could be isolated; therefore, it was inferred that the combination of benzyl radicals with nitric oxide must be very fast. Benzaldehyde was formed in fairly large quantities in the decompositions with and without $\alpha\alpha'$-azoisobutyronitrile, though no mechanism for its formation was postulated.

Bibenzyl was also absent from the decomposition of $\alpha\alpha$-dimethylphenethyl nitrite studied here. The evidence above suggests that reaction between nitric oxide and benzyl radicals is again taking place and our results, together with those of Gingras and Waters,[11] indicate that nitrosotoluene is the precursor of the benzaldehyde. It is known[12] that nitroso-compounds readily rearrange to the corresponding oximes, and therefore the isomerization [reaction (13)] of nitrosotoluene to benzaldoxime may well be an intermediate step:

$$Ph \cdot CH_2 \cdot NO \longrightarrow Ph \cdot CH{:}N \cdot OH \tag{13}$$
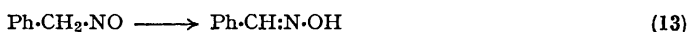
(*d*) Benzoic acid must be formed by the oxidation of benzaldehyde. A similar situation was observed[5] in the thermal decomposition of benzyl nitrite; benzaldehyde, a product of the decomposition, was partially oxidised to benzoic acid. A general mechanism was proposed involving the benzoyl radical as an intermediate which was oxidised to the $Ph \cdot CO_2 \cdot$ radical by nitric or nitrous oxide, the benzoate radical then abstracting hydrogen to give benzoic acid. The present experiments do not shed any further light upon the detailed rôle of the oxides of nitrogen in the oxidation, though it may be significant that large yields of nitrous oxide (accounting for approximately 50% of the nitrogen) were found in the decompositions of $\alpha\alpha$-dimethylphenethyl nitrite in the presence of initially added benzaldehyde; it is probable that some of the nitrous oxide was formed in the oxidation of benzaldehyde.

(*e*) Gaseous products. The production of nitric oxide is explained by the initial step [reaction (1)], although the comparatively small yield (14%) indicates that much of the nitric oxide undergoes subsequent reactions. In particular, nitrous oxide must be formed by the reduction of nitric oxide either directly or *via* the nitroxyl radical [reaction (14)]:

$$2HNO \longrightarrow N_2O + H_2O \tag{14}$$

[11] B. L. Gingras and W. A. Waters, *J.*, 1954, 3508.
[12] B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, **12**, 321.

Nitrogen is formed by reduction of either nitric or nitrous oxide (for possible mechanisms see refs. 5, 6, 9). Carbon dioxide is formed, at least in part, by the decomposition of the benzoate[13] radical:

$$Ph \cdot CO_2 \cdot \longrightarrow Ph \cdot + CO_2 \qquad\qquad (15)$$

Stability of the αα-Dimethylphenethyloxyl Radical.—The experimental results indicate that when decomposition of the αα-dimethylphenethyloxyl radical occurs, it is exclusively by fission of the benzyl–carbon bond. This is, indeed, the mode of decomposition which is favoured thermochemically (by *ca.* 8 to 9 kcal. mole^{-1}):
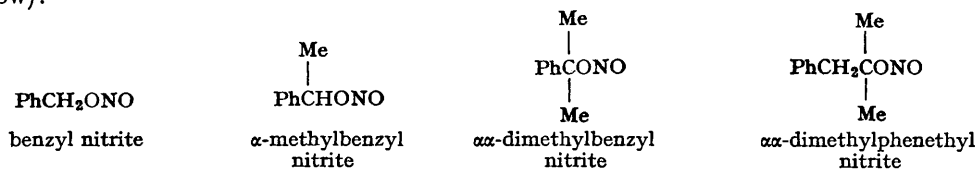
$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot \longrightarrow Ph \cdot CH_2 \cdot + Me_2CO \qquad \Delta H = -4 \cdot 6 \text{ kcal. mole}^{-1}$$

$$Ph \cdot CH_2 \cdot CMe_2 \cdot O \cdot \longrightarrow Me \cdot + Ph \cdot CH_2 \cdot COMe \qquad \Delta H = 3 \cdot 7 \text{ kcal. mole}^{-1}$$

This preferential bond fission has been observed in other systems.[14] Kochi[15] studied the relative rates of elimination of different alkyl groups from various tertiary alkoxyl radicals (which had been formed from alkyl hydroperoxides by redox reactions with metal ions). The influential factor was found to be the bond dissociation energy in the fissionable alkoxyl radical. Benzyl groups were cleaved more rapidly than any n-alkyl radicals, and it is also of interest to note that "concerted" decomposition did not occur in these systems.

It was observed by Kabasakalian *et al.*[2] that the $Ph \cdot CH_2 \cdot CH_2 \cdot O \cdot$ radical, photolytically formed from the corresponding nitrite in benzene solution at ambient temperatures, decomposed to give the benzyl radical and formaldehyde. The homologous $Ph \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot O \cdot$ radical, in contrast, was quite stable, thereby emphasising the readiness with which the benzyl group is eliminated.

However, in addition to decomposition of the αα-dimethylphenethyloxyl radical in this nitrite decomposition, there was considerable "stabilisation" by H-atom abstraction, as revealed by the large yields of 1,1-dimethyl-2-phenylethanol found in the decomposition. The ratio of "stabilisation" to decomposition for the t-alkoxyl radical was 3·5:1 at 151°. This ratio showed appreciable temperature-dependence, the proportion of decomposition becoming greater with increase of temperature. The activation energy for this decomposition was not expected to be greater than 10 kcal. mole^{-1}. It is of interest to note that yields of this same alcohol (though fairly small) have recently been obtained from the thermal decomposition of αα-dimethylphenethyl hydroperoxide[16] in benzene solution.

Comparison of the Decomposition of Aryl-substituted Alkyl Nitrites.—Four aryl-substituted nitrites (benzyl, α-methylbenzyl, αα-dimethylbenzyl, and αα-dimethylphenethyl) have now been the object of detailed pyrolysis studies. Some of the points of especial interest in their decompositions may now be examined in the light of their structural relationship (depicted below):

		Me	Me
	Me	PhCONO	PhCH₂CONO
PhCH₂ONO	PhCHONO	Me	Me
benzyl nitrite	α-methylbenzyl nitrite	αα-dimethylbenzyl nitrite	αα-dimethylphenethyl nitrite

The primary and secondary alkoxyl radicals formed as intermediates in the decomposition of benzyl and α-methylbenzyl nitrites show complete stability toward unimolecular decomposition. Even the 6·8 kcal. enthalpy increase required for fission of the C–Me bond in the 1-phenylethoxyl radical is apparently too great for decomposition to compete effectively with H-abstraction and disproportionation of the alkoxyl radicals. However, in the case of the tertiary alkoxyl radicals there are now three factors which reduce the handicap: the energy requirement of decomposition is decreased; disproportionation cannot take place; because of

[13] C. A. Barson and J. Bevington, *J. Polymer Sci.,* 1956, **20**, 13.
[14] P. Gray and A. Williams, *Chem. Rev.,* 1959, **59**, 239.
[15] J. K. Kochi, *J. Amer. Chem. Soc.,* 1962, **84**, 1193.
[16] R. R. Hiatt and W. M. J. Strachan, *J. Org. Chem.,* 1963, **28**, 1893.

the lack of suitable secondary and tertiary hydrogens, H-atom abstraction is more difficult. Despite these factors, decomposition is not the dominant fate of the two tertiary aryl-substituted alkoxyl radicals. If this is in fact ascribable to the efficiency of HNO in bringing about H-atom transfer in nitrite systems, then formation of the nitroxyl radical may well be related to the considerable degree of nitric oxide reduction encountered in these pyrolyses. Certainly, the nitric oxide released in the initial step of the decomposition is never completely inert in nitrite pyrolyses; even methyl nitrite gives[8] small yields of nitrogen. (Prior to our own work, only 2-octyl[17] of the wholly aliphatic nitrites had been found to give nitrogen, although nitrous oxide formation has been noted in most instances.) The yields of nitric oxide, nitrous oxide, and nitrogen for the four aryl-substituted nitrites are summarised in Table 2. The amount of reduction is quite considerable, molecular nitrogen yields varying from 16 mole per cent for α-methylbenzyl nitrite to 24 mole per cent for benzyl nitrite. (The larger value for benzyl nitrite is a consequence of the oxidation of the benzaldehyde produced to benzoic acid.) The yield of nitrous oxide is always much smaller than the yield of nitrogen and, except for αα-dimethylphenethyl nitrite, is fairly constant. (There, the larger yields of nitrous oxide may be correlated to the oxidation of the benzyl radical to benzaldehyde and benzoic acid.) It is noticeable that the nitric oxide yield is much smaller for the tertiary nitrites than for the primary and secondary nitrites, despite the fact that the extent of reduction to nitrous oxide and nitrogen is similar; this arises because nitric oxide is being captured by alkyl radicals to give nitroso-compounds. One is forced to conclude that the extent of reduction is not merely a function of the class of nitrite (primary, secondary, or tertiary), but also depends upon the precise groups present.

TABLE 2.

Yields of nitrogen-containing gases from the thermal decomposition of aryl-substituted alkyl nitrites (product yields expressed in moles per 100 moles nitrite).

Nitrite	NO	N_2O	N_2	% NO reduced to $N_2O + N_2$
Benzyl	36	2	24	52
α-Methylbenzyl	56	2	16	36
αα-Dimethylbenzyl	8	2·5	21	47
αα-Dimethylphenethyl	13	8	20	56

Autocatalysis is displayed by all four decompositions. The largest catalytic effects are observed where benzaldehyde is a prominent product, when its artificial addition increases the reaction velocity many-fold. A subsidiary contribution to autocatalysis in the decomposition of the tertiary nitrites may arise from a chain reaction made possible by the attack of alkyl radicals on the original nitrite, for the tertiary alkoxyl radicals are the least stable and capable of giving rise to free alkyl radicals by their decomposition.

Finally, there are the contributions of intermolecular and intramolecular effects to the observed rates of decomposition. The same O–N bonds are broken in all cases, but the rates of decomposition of the two tertiary nitrites are much less than those of the primary and secondary nitrites. It has already been pointed out that the tertiary nitrites form a less reactive solvent cage for the alkoxyl and nitric oxide radicals so that recombination occurs, and that their decomposition is only rapid in cages of cumene or benzaldehyde. Cage effects are *intermolecular* contributions; to them must be added *intramolecular* influences. The tertiary alkoxyls, unlike the primary and secondary radicals, cannot undergo decomposition by disproportionation to carbonyl plus alcohol and it is as a consequence of both these factors that the differences in rates of reaction and alcohol yields shown by the tertiary nitrites arise.

PHYSICAL CHEMISTRY DEPARTMENT
THE UNIVERSITY, LEEDS 2.

[17] N. Kornblum and E. P. Oliveto, *J. Amer. Chem. Soc.*, 1949, **71**, 226.