13. Photofragmentation of Dibenzyl Ketone in the Presence of Tetramethylpiperidine Derivatives.

Studies on Light Stabilizer Mechanisms [1]

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Summary

The interaction of selected tetramethylpiperidine derivatives with radicals arising from the *Norrish*-type I cleavage of dibenzyl ketone under oxygen was studied. Product analyses and kinetic studies showed that the investigated sterically hindered piperidine derivatives have a pronounced effect on both the nature and distribution of the products of photolysis of dibenzyl ketone in the presence of oxygen. Observations indicated that the phenylperacetoxyl radical is formed as an intermediate during irradiation and that it interacts with the additives used. Possible mechanisms of the reactions studied are discussed.

The observation that oxidation of an isolated double bond by the radicals formed in dibenzyl ketone photolysis under oxygen is strongly inhibited in the presence of the studied sterically hindered amines is discussed in the light of the results presented. The findings are considered in relation to the problem of polymer stabilization.

Introduction. - Certain sterically hindered amines (HALS = Hindered Amine Light Stabilizer) have a light-stabilizing action on various polymers (*e.g.*, polyolefins, styrol polymers, polyurethanes) which is far superior to that of any of the stabilizing systems so far used [2-9]. The mode of action of this technically and scientifically interesting group of substances has already been the subject of many publications [10-20].

As all these studies have shown, hindered amines and their derivatives do not act as UV. absorbers. Also they only play a secondary role as quenchers of excited carbonyl groups and singlet oxygen [11-13] [21] [22]. For this reason, attention was turned at a fairly early stage to the radical-scavenging action of hindered piperidines and especially their nitroxyl derivatives [10] [14]. In the main, interest was centred on the reaction of the nitroxyl with alkyl radicals giving rise to hydroxylamine ethers and the cleavage of the latter by peroxyl radicals [14] [20] (reaction (1)).

$$\rangle NO^{\cdot} + R^{\cdot} \longrightarrow \rangle NOR \xrightarrow{R'OO^{\cdot}} \rangle NO^{\cdot} + ROOR' \qquad (1)$$

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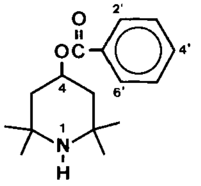
We have studied the interactions between tetramethylpiperidine derivatives and further oxygen centred radicals produced by ketone photolysis. It is known that the oxidation of polymers gives rise to ketones that undergo *Norrish*-type I and II cleavage on exposure to light. Although ketone photolysis in an inert atmosphere has been extensively studied [23-26], much less work - with the exception of polymer photo-oxidation studies - has been done on the irradiation of ketones in oxidizing media [27-30]. The present study is concerned mainly with the interaction between sterically hindered piperidine derivatives and the radicals formed in *Norrish*-type I cleavage of a model ketone (dibenzyl ketone = DBK) in the presence of oxygen. Dibenzyl ketone, whose photochemistry in an inert atmosphere is fairly well known [31-35], is characterized by a *Norrish*-type I cleavage with a high quantum yield ($\Phi = 0.7$ [32] [33]) which makes this compound of special interest as a convenient source of radicals.

Similar studies on the purely aliphatic compound diisopropyl ketone (DIPK) [36], which is structurally closer to the carbonyl groups likely to be present in polyolefins, have supplemented and largely confirmed the results obtained in the present study of DBK photo-oxidation (in this work the term DBK photo-oxidation is used for DBK photolysis in the presence of oxygen).

The oxygen-centred radicals arising in DBK photo-oxidation are capable of oxidizing isolated double bonds, and this oxidation is inhibited in the presence of sterically hindered amines [1].

Kinetic studies and product analyses, which will be described in this paper, have shown that the investigated sterically hindered piperidines have a marked effect on the yield and distribution of the products of DBK photolysis in the presence of oxygen. 4-Benzoyloxy-2,2,6,6-tetramethylpiperidine (**1**) ($>$NH) and 4-benzoyloxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (**2**) ($>$NO$^{\cdot}$) were used as model piperidines. The results obtained so far in this and earlier studies are discussed in relation to possible modes of action of HALS.



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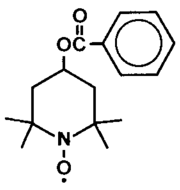

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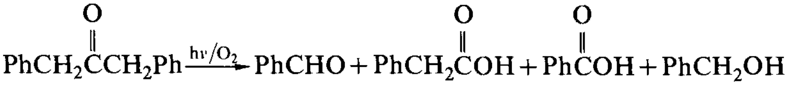
Results. - For radical reactions in the presence of oxygen a complex mixture of products is to be expected. In fact, as *Figure 1* shows, at least four products can be identified for DBK photo-oxidation, the amounts of which stand in no stoichiometric relationship to the amount of dibenzyl ketone (**3**) decomposed. They are benzaldehyde (**4**), phenylacetic acid (**5**), benzoic acid (**6**) and benzyl alcohol (**7**) (reaction (2)):



$$\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph \xrightarrow{h\nu/O_2} PhCHO + PhCH_2\overset{O}{\overset{\|}{C}}OH + Ph\overset{O}{\overset{\|}{C}}OH + PhCH_2OH} \qquad (2)$$

3 **4** **5** **6** **7**

In *Figures 1-3*, the increase in concentration of the products formed is shown as a function not of the irradiation time but of the relative decrease in the amount of DBK, *i.e.* of $1-([\mathrm{DBK}]_t/[\mathrm{DBK}]_0)$. This method of plotting provides a measure of radical formation[1]).

From the nature of the products formed (benzaldehyde, benzoic acid), it is clear that radicals formed after α-cleavage are taken up by the oxygen and then react further. The appearance of phenylacetic acid on the other hand indicates that the primarily formed phenylacetyl radical is at least in part taken up directly by the oxygen.

In the presence of hindered piperidine derivatives studied the pattern of DBK photo-oxidation becomes considerably simpler. We consider first the results obtained with nitroxyl **2**. *Figure 2* shows the course of DBK photolysis in the presence of oxygen and **2**. Benzaldehyde (**4**) and phenylacetic acid (**5**) are now the main products, the former corresponding to 100% and the latter to 80% of the amount of DBK decomposed. Benzoic acid, formed in small quantities in DBK photolysis without additive, also arises in this reaction, though in still smaller

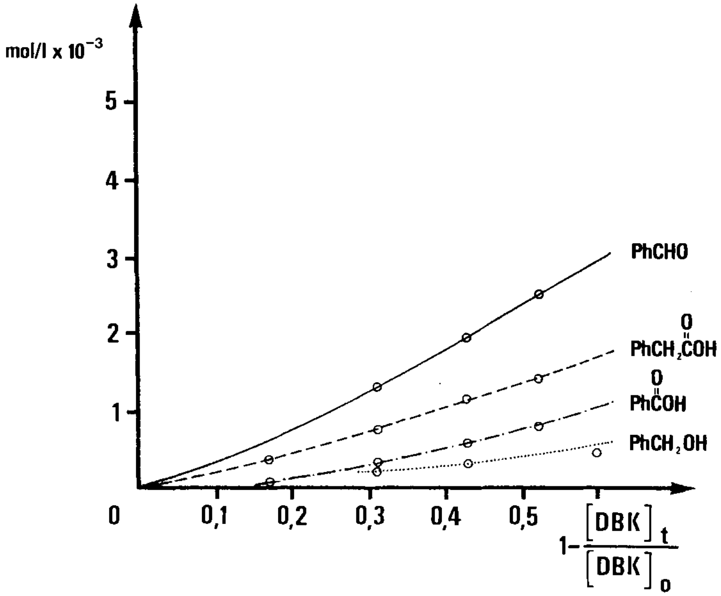


Figure 1. *Photo-oxidation of DBK in benzene.* Formation of products as a function of DBK decrease $(1-[\mathrm{DBK}]_t/[\mathrm{DBK}]_0)$; $[\mathrm{DBK}]_0 = 10^{-2}$ mol/l.

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[1]) If we denote the total rate of radical formation at time t by $B(t) = -d[\mathrm{DBK}]_t/dt$, then $[\mathrm{DBK}]_0 - [\mathrm{DBK}]_t = \int_0^t B(t)dt$ or $1-([\mathrm{DBK}]_t/[\mathrm{DBK}]_0) = (\int_0^t B(t)dt)/[\mathrm{DBK}]_0$.

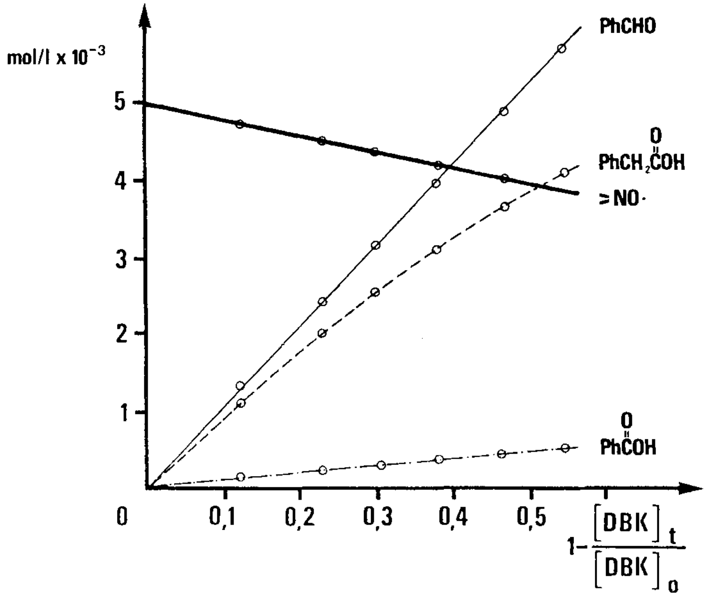
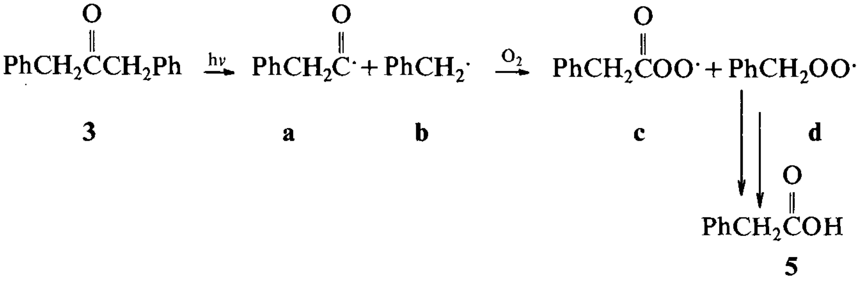


Figure 2. *Photo-oxidation of DBK in the presence of* **2**. $[DBK]_0 = 10^{-2}$ mol/l, $[{>}NO^{\cdot}]_0 = 5 \times 10^{-3}$ mol/l (in benzene)

amount corresponding to less than 10% of the main products. The high yield of phenylacetic acid shows that in the presence of the stable nitroxyl, decarbonylation of the phenylacetyl radical [33] - a process with a high rate constant - is largely suppressed. Apparently the phenylperacetoxyl radical is first formed by addition of oxygen. In the presence of the nitroxyl **2** this then gives rise, *via* a non-oxidative and non-fragmenting reaction, to phenylacetic acid (reaction (3)).



$$\underset{\mathbf{3}}{\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph}} \xrightarrow{h\nu} \underset{\mathbf{a}}{\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}{\cdot}}} + \underset{\mathbf{b}}{\mathrm{PhCH_2{\cdot}}} \xrightarrow{O_2} \underset{\mathbf{c}}{\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}OO{\cdot}}} + \underset{\mathbf{d}}{\mathrm{PhCH_2OO{\cdot}}} \quad (3)$$

$$\downarrow\downarrow \quad \underset{\mathbf{5}}{\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}OH}}$$

Isolation of the corresponding recombination products **8** and **9** according to reaction (4) led to the conclusion that the phenylacetyl and benzyl radicals **a** and **b** were the initial species arising from DBK photolysis[2]).

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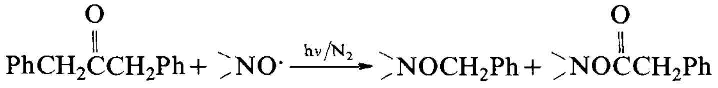
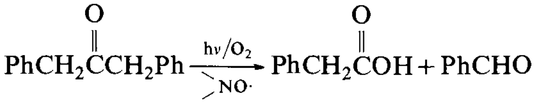
[2]) *Robbins & Eastman* [37] assumed the presence of radicals **a** and **b** on the basis of NMR. data measured *in situ* on their recombination products with a stable nitroxyl radical.



$$\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph + {>}NO^{\cdot} \xrightarrow{h\nu/N_2} {>}NOCH_2Ph + {>}NO\overset{O}{\overset{\|}{C}}CH_2Ph} \qquad (4)$$

3 **2** **8** **9**

In a purely formal way, the formation of the substances identified as main products in *Figure 2* can be summarized by reaction (5):



$$\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph \xrightarrow[{>}NO^{\cdot}]{h\nu/O_2} PhCH_2\overset{O}{\overset{\|}{C}}OH + PhCHO} \qquad (5)$$

3 **5** **4**

The individual steps in this reaction will be discussed later in this paper. Here we draw attention to an important characteristic of reaction (5), namely the fact that the amount of additive **2** present in the reaction mixture decreases to a relatively small extent during the reaction (*ca.* 10% of the total radical formation) despite the considerable influence it has on the reaction as a whole. It follows that this influence must be of a catalytic nature.

Of technical interest for light stabilization of plastics are not, however, the coloured nitroxyl radicals but above all the suitably substituted, colourless, sterically hindered amines. The effect of one such substance (**1**), on DBK photolysis

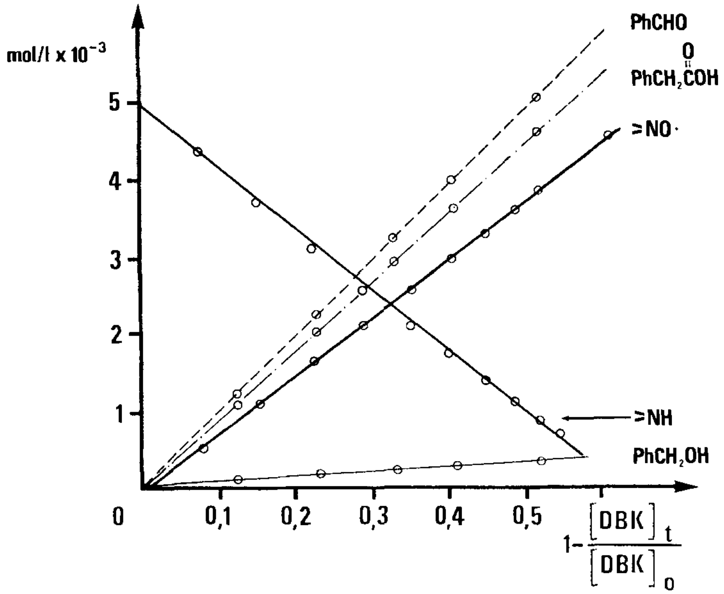
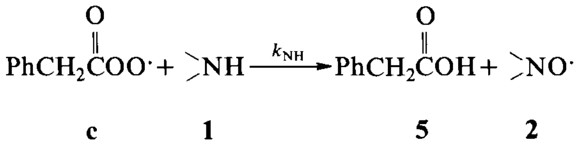


Figure 3. *Photo-oxidation of DBK in the presence of* **1**. [DBK]$_0$ = 10^{-2} mol/l, [>NH]$_0$ = 5 × 10^{-3} mol/l (in benzene)

under oxygen is shown in *Figure 3.* The amine also affects the course of the reaction, *i.e.* the ketone is converted almost quantitatively into benzaldehyde and phenylacetic acid, while at the same time the amine disappears at a rate nearly equivalent to that of DBK fragmentation, with formation of the corresponding nitroxyl **2**. The amount of nitroxyl formed is equivalent to *ca.* 80% of the amount of DBK irradiated, *i.e.* the nitroxyl formed will at best be equivalent to half the amount of radicals arising from cleavage of the DBK (a small proportion of the nitroxyl is consumed irreversibly in secondary reactions, see *Fig. 2*). Even under modified experimental conditions the relationship $\Delta[\text{DBK}]/\Delta[\mathbf{1}] \sim 1$ is maintained *(Table).* This observation strongly suggests that of the two peroxyl radicals formed (reaction (3)), only one is responsible for oxidation of the amine. Taking into account the equivalence between amine decrease and nitroxyl formation, the following reactions (6) and (7) can be considered:



$$\underset{\mathbf{c}}{PhCH_2\overset{\overset{O}{\|}}{C}OO^{\cdot}} + \underset{\mathbf{1}}{>NH} \xrightarrow{k_{NH}} \underset{\mathbf{5}}{PhCH_2\overset{\overset{O}{\|}}{C}OH} + \underset{\mathbf{2}}{>NO^{\cdot}} \tag{6}$$

$$\underset{\mathbf{d}}{PhCH_2OO^{\cdot}} + \underset{\mathbf{1}}{>NH} \longrightarrow \underset{\mathbf{7}}{PhCH_2OH} + \underset{\mathbf{2}}{>NO^{\cdot}} \tag{7}$$

From the nature of the reaction products *(Fig. 3)*, it is much more likely that the amine is oxidized by the phenylperacetoxyl radical **c** than by the benzylperoxyl radical **d**. Further support for reaction (6) was given by the following experiments.

The benzylperoxyl radical was produced independently by photolysis of di-*t*-butyl peroxide (**10**) in the presence of toluene (**11**) and oxygen (reactions (8)-(10)).

$$\underset{\mathbf{10}}{(CH_3)_3COOC(CH_3)_3} \xrightarrow{h\nu} 2\,(CH_3)_3CO^{\cdot} \tag{8}$$

$$(CH_3)_3CO^{\cdot} + \underset{\mathbf{11}}{PhCH_3} \longrightarrow (CH_3)_3COH + \underset{\mathbf{b}}{PhCH_2^{\cdot}} \tag{9}$$

$$\underset{\mathbf{b}}{PhCH_2^{\cdot}} + O_2 \longrightarrow \underset{\mathbf{d}}{PhCH_2OO^{\cdot}} \tag{10}$$

Table

$[DBK]_o$	$[1]_o$	$[DBK]_o/[1]_o$	$\Delta[DBK]/\Delta[1]$
10^{-2} mol/l	5×10^{-3} mol/l	2	1.3
10^{-2}	10^{-2}	1	1.2
10^{-2}	5×10^{-2}	0.2	0.9

The effectiveness of the benzylperoxyl radical **d** as oxidizing agent was tested by adding the amine **1** to the reaction mixture and studying its oxidation to the nitroxyl **2**. *Figure 4* shows the formation of **2** in toluene as a function of benzylperoxyl radical formation according to reactions (8)-(10) (curve A) and as a function of radical production during DBK irradiation (curve B). The amine is much more rapidly oxidized *via* DBK photolysis (comparison is made between the initial reaction rates, shown by the broken lines, since later the processes are influenced by secondary reactions). An additional experiment further showed that the rate of amine oxidation is the same in toluene as in benzene *(Fig. 5)*. We conclude that the benzylperoxyl radical **d** contributes little (*ca.* 10%) to oxidation of the amine and that the peracetoxyl radical **c** is responsible for this fast oxidation.

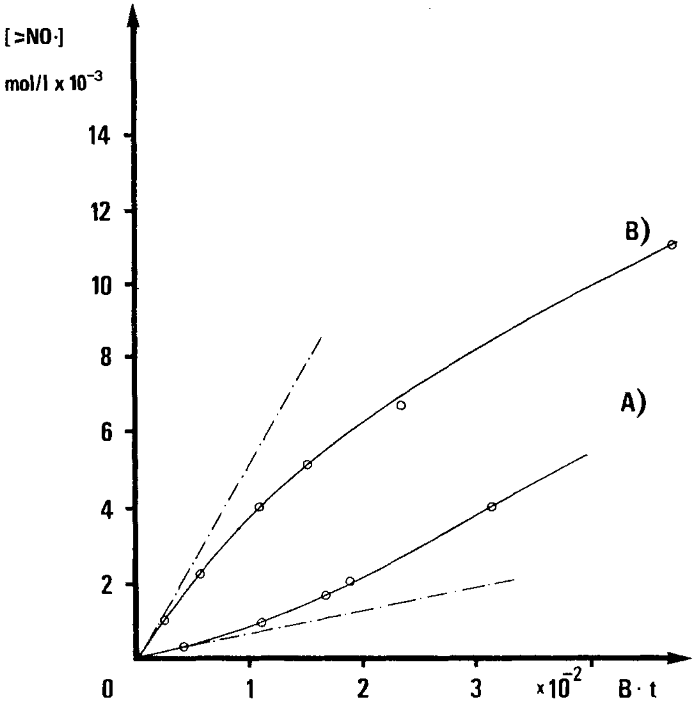


Figure 4. *Formation of* **2** *from* **1** *in toluene during benzylperoxyl radical production according to reactions (8)-(10) (curve A) and during DBK photo-oxidation (curve B).* $[(CH_3)_3COOC(CH_3)_3]_o = 2$ mol/l, $[DBK]_o = 10^{-2}$ mol/l. B = rate of radical formation, mol/l · s; [t] = s; broken lines: initial rate

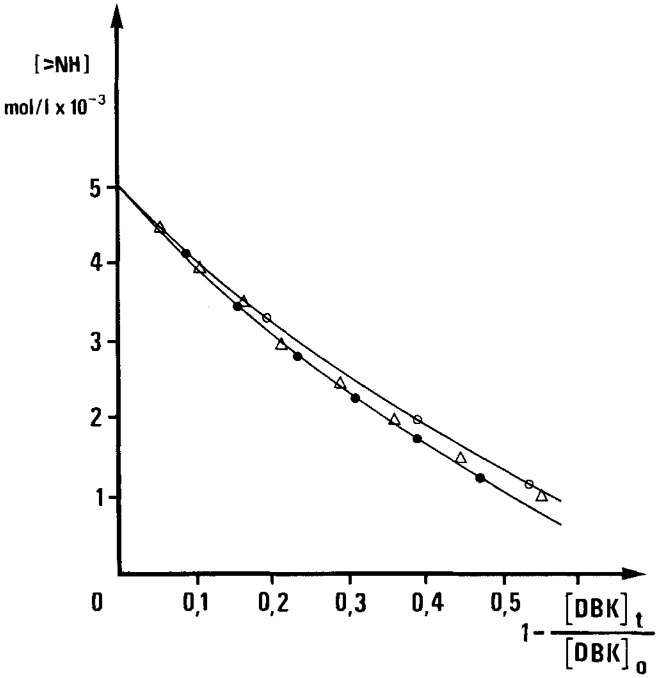
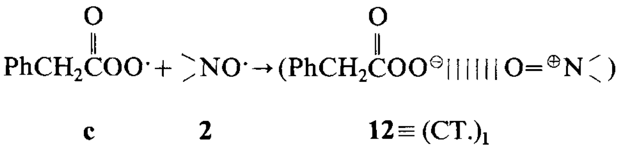


Figure 5. *Decrease of concentration of* **1** *as a function of DBK photo-oxidation.* $[DBK]_0 = 10^{-2}$ mol/l. –●–: in benzene, –○–: in toluene, –△–: calculated according to equation (16) with $k_5/k_{NH} = 0.4$

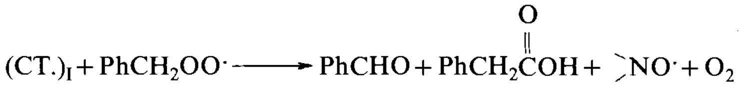
Discussion. – *A. Interpretation of the experimental results.* The studied tetramethylpiperidine derivatives **1** and **2** are capable of affecting the distribution of the products of DBK photo-oxidation to a very marked extent. The observed uniformity of the products, as well as the fact that the nitroxyl radical emerges from the reaction almost unchanged, point to a mechanism in which all the radicals are involved but which proceeds specifically with regeneration of the nitroxyl. For this reason we propose first to discuss the reaction mechanism in the presence of **2**. Comparison of *Figures 1* and *2* shows that this radical strongly affects the yield of phenylacetic acid. In principle there are various ways of accounting for the quantitative formation of this acid. The results can be explained kinetically by any reaction involving **2** and either the benzylperoxyl or phenylperacetoxyl radical, giving rise to a transient species which is oxidized as soon as it is formed by the second peroxyl radical with the appearance of benzaldehyde and phenylacetic acid and release of **2**. The most probable mechanisms will now be discussed.

One of the possibilities is stabilization of the phenylperacetoxyl radical **c** by the nitroxyl with formation of a charge-transfer complex **12** (CT.) (reaction (11)).



$$\underset{\mathbf{c}}{PhCH_2\overset{\overset{\large O}{\|}}{C}OO^{\cdot}} + \underset{\mathbf{2}}{>NO^{\cdot}} \rightarrow \underset{\mathbf{12} \equiv (CT.)_1}{(PhCH_2\overset{\overset{\large O}{\|}}{C}OO^{\ominus}|||||O{=}^{\oplus}N<)} \qquad (11)$$

In a second step this complex reacts with a benzylperoxyl radical (reaction (12), reaction (11)+(12)= variant A).



$$(\mathrm{CT.})_{\mathrm{I}} + \mathrm{PhCH_2OO^{\cdot}} \longrightarrow \mathrm{PhCHO} + \mathrm{PhCH_2\overset{\overset{\large O}{\|}}{C}OH} + \mathrm{>NO^{\cdot}} + \mathrm{O_2} \qquad (12)$$

12 **d** **4** **5** **2**

Kinetically equivalent to this picture is the interchange of radicals in reactions (11) and (12), *i.e.* formation of a CT. complex **13** between the benzylperoxyl radical **d** and the nitroxyl **2** (reactions (11′)+(12′)= variant B).

$$\mathrm{PhCH_2OO^{\cdot}} + \mathrm{>NO^{\cdot}} \longrightarrow (\mathrm{PhCH_2OO^{\ominus}}\,||||||\,\mathrm{O{=}^{\oplus}N}\!<) \qquad (11')$$

d **2** **13**$\equiv(\mathrm{CT.})_{\mathrm{II}}$

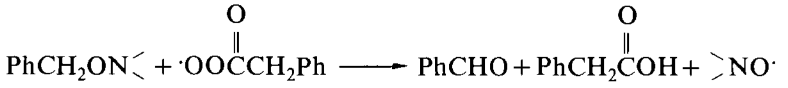
$$(\mathrm{CT.})_{\mathrm{II}} + \mathrm{PhCH_2\overset{\overset{\large O}{\|}}{C}OO^{\cdot}} \longrightarrow \mathrm{PhCHO} + \mathrm{PhCH_2\overset{\overset{\large O}{\|}}{C}OH} + \mathrm{>NO^{\cdot}} + \mathrm{O_2} \qquad (12')$$

13 **c** **4** **5** **2**

A further possibility would be formation not of a CT. complex but of a stable product, namely >NO-benzyl **8** (reaction (13)). This again would be quantitatively oxidized by peracetoxyl radicals **c** with formation of phenylacetic acid (**5**) (reaction (14)= variant C).

$$\mathrm{PhCH_2OO^{\cdot}} + \mathrm{>NO^{\cdot}} \longrightarrow \mathrm{PhCH_2ON}\!< + \mathrm{O_2} \qquad (13)$$

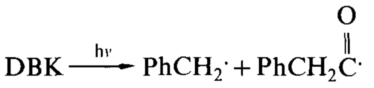
d **2** **8**



$$\mathrm{PhCH_2ON}\!< + \mathrm{{}^{\cdot}OO\overset{\overset{\large O}{\|}}{C}CH_2Ph} \longrightarrow \mathrm{PhCHO} + \mathrm{PhCH_2\overset{\overset{\large O}{\|}}{C}OH} + \mathrm{>NO^{\cdot}} \qquad (14)$$

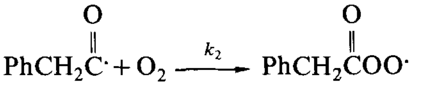
8 **c** **4** **5** **2**

The first two variants are fully compatible with our experimental results. This can best be demonstrated on the example of variant A (reactions (11)/(12)), for which we can postulate the following set of reactions:



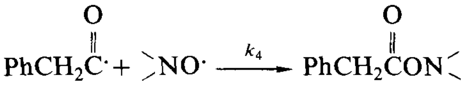
$$\mathrm{DBK} \xrightarrow{h\nu} \mathrm{PhCH_2^{\cdot}} + \mathrm{PhCH_2\overset{\overset{\large O}{\|}}{C}{}^{\cdot}} \qquad (\mathrm{I})$$

$$\mathrm{PhCH_2^{\cdot}} + \mathrm{O_2} \xrightarrow{k_{\mathrm{I}}} \mathrm{PhCH_2OO^{\cdot}} \qquad (\mathrm{II})$$



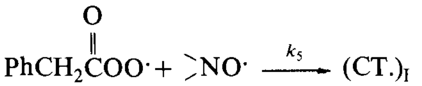
$$PhCH_2\overset{\overset{O}{\|}}{C}{}^{\cdot} + O_2 \xrightarrow{k_2} PhCH_2\overset{\overset{O}{\|}}{C}OO^{\cdot} \qquad (III)$$

$$PhCH_2^{\cdot} + {>}NO^{\cdot} \xrightarrow{k_3} PhCH_2ON{<} \qquad (IV)$$

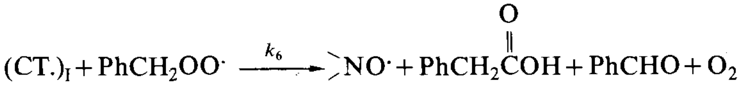


$$PhCH_2\overset{\overset{O}{\|}}{C}{}^{\cdot} + {>}NO^{\cdot} \xrightarrow{k_4} PhCH_2\overset{\overset{O}{\|}}{C}ON{<} \qquad (V)$$

Remarks on (II)-(V): k_1 and k_2 are so large that with oxygen saturation the recombination of $PhCH_2^{\cdot}$, and the recombination or decarbonylation of $PhCH_2CO^{\cdot}$, can be neglected. However, a reaction with ${>}NO^{\cdot}$ that is to some extent competitive cannot be ruled out.

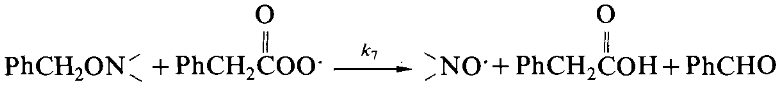


$$PhCH_2\overset{\overset{O}{\|}}{C}OO^{\cdot} + {>}NO^{\cdot} \xrightarrow{k_5} (CT.)_I \qquad (cf.\ \text{reaction (11)}) \qquad (VI)$$



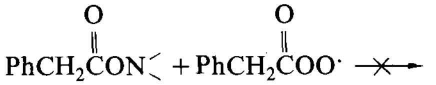
$$(CT.)_I + PhCH_2OO^{\cdot} \xrightarrow{k_6} {>}NO^{\cdot} + PhCH_2\overset{\overset{O}{\|}}{C}OH + PhCHO + O_2 \qquad (VII)$$

$$(cf.\ \text{reaction (12)})$$



$$PhCH_2ON{<} + PhCH_2\overset{\overset{O}{\|}}{C}OO^{\cdot} \xrightarrow{k_7} {>}NO^{\cdot} + PhCH_2\overset{\overset{O}{\|}}{C}OH + PhCHO \qquad (VIII)$$

$$(cf.\ \text{reaction (14)})$$



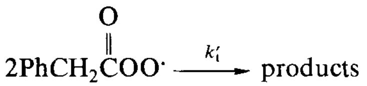
$$PhCH_2\overset{\overset{O}{\|}}{C}ON{<} + PhCH_2\overset{\overset{O}{\|}}{C}OO^{\cdot} \not\longrightarrow \qquad (IX)$$

$$PhCH_2ON{<} + PhCH_2OO^{\cdot} \not\longrightarrow \qquad (X)$$

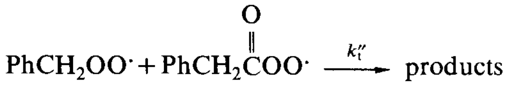
Remarks on (VIII)-(X): Supplementary experiments have shown ${>}NO$-benzyl but not ${>}NO{-}CO$-benzyl is oxidized by the peracetoxyl radical. Under our experimental conditions (RT.) however, there was no notable oxidation of $PhCH_2ON{<}$ by $PhCH_2OO^{\cdot}$.

$$2PhCH_2OO^{\cdot} \xrightarrow{k_t} 2PhCHO + \text{unknown products} \qquad (XI)$$

Remarks on (XI): Experiments in which benzylperoxyl radicals alone were produced in accordance with reactions (8)-(10) showed quite clearly that the termination of these radicals results selectively in benzaldehyde and not the benzyl alcohol that would also be expected from the *Russell* mechanism [38].

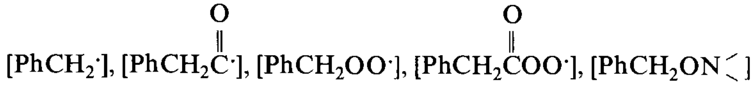


$$2PhCH_2\overset{\overset{O}{\|}}{C}OO^{\cdot} \xrightarrow{k_t'} \text{products} \qquad (XII)$$



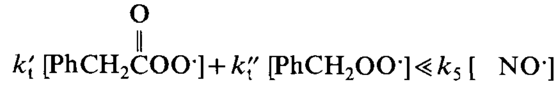
$$PhCH_2OO\cdot + PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}OO\cdot \xrightarrow{k_t''} \text{products} \qquad \text{(XIII)}$$

Under the usual assumption of stationary conditions for



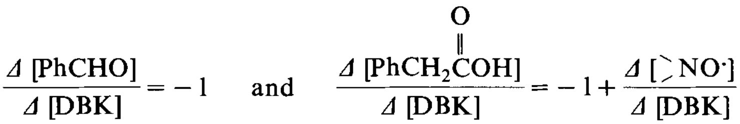
$$[PhCH_2\cdot], [PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}\cdot], [PhCH_2OO\cdot], [PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}OO\cdot], [PhCH_2ON\langle]$$

and the charge-transfer complex $(CT.)_{II}$, and assuming that



$$k_t' [PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}OO\cdot] + k_t'' [PhCH_2OO\cdot] \ll k_5 [\ \ NO\cdot]$$

we obtain the following linear relationships from this model:



$$\frac{\Delta\,[PhCHO]}{\Delta\,[DBK]} = -1 \quad \text{and} \quad \frac{\Delta\,[PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}OH]}{\Delta\,[DBK]} = -1 + \frac{\Delta\,[>NO\cdot]}{\Delta\,[DBK]}$$

with $\Delta\,[DBK] = [DBK]_t - [DBK]_o$

These equations describe very closely the experimental findings *(Fig. 2)*. The loss of **2** is accounted for by reaction with the acyl radical in accordance with reaction (V).

Variant C (reactions (13)/(14)) would also explain the quantitative formation of the products in analogous fashion (in the reaction set (I)-(XIII), (VII) must be omitted and (VI) replaced by (VI′)):

$$PhCH_2OO\cdot + >NO\cdot \xrightarrow{k_5'} PhCH_2ON \ \ + O_2 \qquad \text{(VI′)}$$

For this case the analysis results in the following relation

$$k_5' \, [PhCH_2OO\cdot]\,[>NO\cdot] \sim B_{PhCH_2OO\cdot}$$

where $B_{PhCH_2OO\cdot}$ = rate of formation of the peroxyl radicals. This means that as soon as they are formed, the benzylperoxyl radicals must be captured by the nitroxyl, which is contrary to the experimental findings: when namely benzyl or benzylperoxyl radicals are produced in accordance with reactions (8)-(10), it follows from *Figure 6* that the loss of nitroxyl would be much less in the presence of benzylperoxyl radicals than in the presence of benzyl radicals, which are rapidly and quantitatively captured by **2**. The third reaction variant can therefore be ruled out.

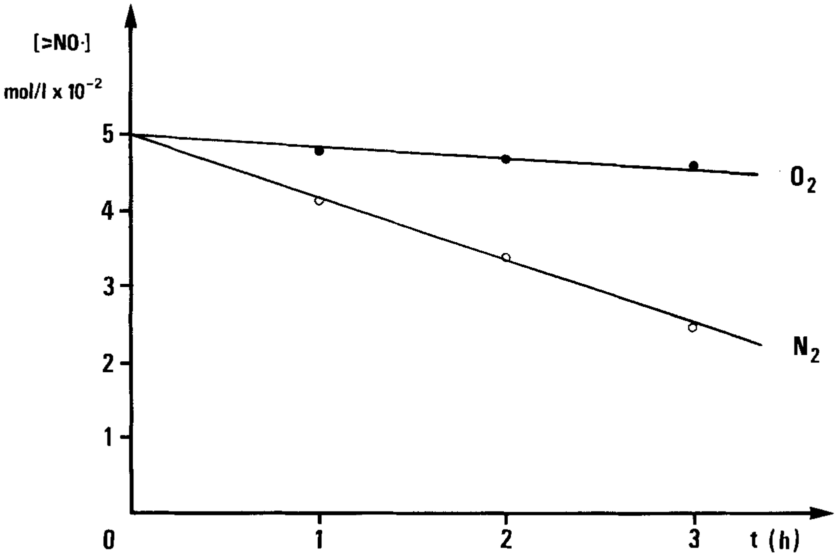
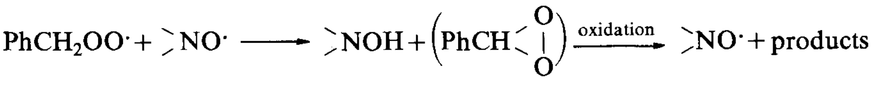


Figure 6. *Decrease of concentration of* **2** *during the photolysis of* $(CH_3)_3COOC(CH_3)_3$ *in the presence of* N_2 (–○–) *and* O_2 (–●–). $[(CH_3)_3COOC(CH_3)_3] = 2$ mol/l; $[\gt NO^\cdot]_0 = 5 \times 10^{-2}$ mol/l

Instead of $\gt NOCH_2Ph$ (**8**) the intermediate formation of the hydroxylamine **14** as a transient species could also be considered, *e.g.* by reaction (15):

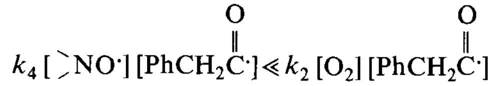


$$PhCH_2OO^\cdot + \gt NO^\cdot \longrightarrow \gt NOH + \left(PhCH\begin{smallmatrix} O \\ | \\ O \end{smallmatrix}\right) \xrightarrow{\text{oxidation}} \gt NO^\cdot + \text{products} \qquad (15)$$

d **2** **14** ? **2**

(Separate experiments on reactions of $\gt NOH$ show that this compound can be very easily converted to nitroxyl by peroxyl radicals or even oxygen). A reaction path leading exclusively to the experimentally observed quantitative formation of phenylacetic acid and benzaldehyde seems to us rather unlikely, however, in this way.

When the amine **1** is added in DBK photo-oxidation phenylacetic acid and benzaldehyde likewise arise in proportion to the loss of the ketone, with almost simultaneous formation of **2**. This result is consistent with a fast and dominating reaction between the phenylperacetoxyl radical and the amine according to reaction (6), if we assume that the simultaneous and quantitative formation of benzaldehyde mainly originates from recombination of benzylperoxyl radicals. As we have already pointed out in the discussion on the mechanism operative in the presence of **2** (reaction (XI)), recombination of benzylperoxyl radicals under our experimental conditions obviously does not follow the course described by *Russell* [38]. The approximately linear amine decrease is slightly smaller than the corresponding phenylacetic acid formation *(Fig. 3)*. A more accurate inspection of the amine oxidation *(Fig. 5)* even indicates a slight retardation of the amine decrease with increasing DBK photolysis. This observation may be explained on the basis of the interactions between **2** and peroxyl radicals already discussed (reactions (11)/(12) or (11')/(12')), which compete with the oxidation of amine by peracetoxyl radical. Because of this competition the steadily increasing concentration of nitroxyl formed in the course of the reaction would increasingly slow down the rate of amine oxidation. When reaction (6) (reaction velocity constant $= k_{NH}$) is combined with reactions (I)-(XIII), and



$$k_4[\rangle NO^\cdot][PhCH_2\overset{\overset{O}{\|}}{C}{}^\cdot] \ll k_2[O_2][PhCH_2\overset{\overset{O}{\|}}{C}{}^\cdot]$$

we obtain the approximate relationship

$$\left(1-\frac{[DBK]_t}{[DBK]_0}\right) \sim \frac{[NH]_0}{[DBK]_0}\left\{\left(1-\frac{k_5}{k_{NH}}\right)\left(1-\frac{[NH]}{[NH]_0}\right)-\frac{k_5}{k_{NH}}\ln\frac{[NH]}{[NH]_0}\right\} \quad (16)$$

As a result of the tem $-k_5/k_{NH}$ ln $[NH]/[NH]_0$, a deviation of the decrease of **1** from linearity and thus a continuous slowing-down of amine oxidation is to be anticipated when the ratio of k_5 to k_{NH} is sufficiently large. From our measurements we conclude that the rate of amine oxidation in reaction (6) is considerably higher than that of the possibly competitive reaction (11). A ratio of $k_5/k_{NH} \sim 0.4$ is compatible with our experimental curves (see *Fig. 5*).

We now briefly discuss another possible explanation for the nature of the products found which does not involve intervention of free radicals. In their work on olefin oxidation sensitized by special ketones [29] [30] *Bartlett et al.* drew attention to the formation of a complex between the excited ketone and oxygen which could give rise to further reactions. Unlike these workers, however, we found that the ketone used by us could not be recovered undecomposed. In our case an exiplex could possibly be formed between the excited DBK and oxygen or nitroxyl. This exiplex would then have to react with the remaining groups ($\rangle NO^\cdot$ or O_2), with simultaneous breakdown of the resulting complexes and formation of the products actually found. In view of the nature of the latter, such a reaction pattern can be satisfactorily formulated with the nitroxyl **2** but not with the amine **1**.

B. *Mechanism of inhibition of olefin oxidation by HALS [1].* Earlier studies in which oxygen centred radicals produced by photo-oxidation of DBK were used to oxidize isolated double bonds showed that hindered piperidine derivatives had a very marked influence on that reaction [1].

In this case too it was possible to show by supplementary experiments (reactions (8)-(10)) that the radical responsible for oxidation of the double bond is not the benzylperoxyl but the peracetoxyl radical. Bearing in mind the interaction between the hindered amines studied and peroxyl radicals discussed previously, the observed inhibition of olefin oxidation by these additives can be explained as follows: both interactions (reactions (11)/(12) and (6)) result in continuous consumption of the peracetoxyl radical, a reaction that competes strongly with the olefin oxidation. The most interesting feature of the latter reaction is the fact that both **1** and **2** are capable of inhibiting the double bond oxidation at concentrations that are nearly catalytic (5×10^{-5} mol/l). In the case of **2**, this could be the result of a regeneration mechanism as shown in reactions (11)/(12) or (11')/(12').

C. *Significance of the findings for the light stabilization of polymers.* When DBK is irradiated in the presence of oxygen under the conditions described (DBK in solution, oxygen saturation), there is almost quantitative oxidation of the added amine to the corresponding nitroxyl in amount equivalent to radical formation. In polymers, however, the situation as regards conversion of amines into nitroxyl radicals differs considerably from that in our model experiments. Irradiation of polyethylene and polybutadiene sheets (in air) to which sterically hindered amines had been applied at various concentrations showed that the maximum nitroxyl concentration reached in no case exceeded *ca.* 1-2% of the amine concentration used. That is to say, when stabilization was carried out with the 0.5% of amine usual in practice ($\sim 2 \times 10^{-2}$ mol/kg for amine **1** for example), the nitroxyl concentration does not exceed *ca.* 0.01% ($\sim 4 \times 10^{-4}$ mol/kg for **2** for example). Similar observations have been made by other workers on polypropylene [15] [20] [39] and nitrile rubber [15] [40]. What relevance have the results of model studies to polymer photo-oxidation and stabilization? Here we must stress that the studies reported were confined to only one aspect of the whole subject of polymer photo-oxidation. In practice, in addition to ketone photolysis, photolytic cleavage of hydroperoxides and peroxides must be taken into account when studying polymer oxidation [41] [42]. This gives rise to further species of radicals (*e.g.* $HO^{\cdot}$, $RO^{\cdot}$), so we cannot exclude the possibility at least of reactions of these with amines that do not result in the formation of nitroxyl radicals. Moreover, for the sake of clarity, our experiments were carried out under conditions of oxygen saturation, whereas in practice the photo-oxidation of polymer samples is performed under only partial oxygen saturation. In polymers therefore, the addition of alkyl radicals to the nitroxyl formed from the amine plays a more important role than in our model studies. For all these reasons it was to be expected *a priori* that the ratio [amine]/[nitroxyl] in polymers would not be the same as in the model.

In the field of polymer stabilization, a contribution has at least been made to preventing oxidation of double bonds by the interactions studied, namely peracetoxyl radical/amine and peroxyl radicals/nitroxyl. In polydiene polymers this can play an important role, in polyolefins (terminal double bonds) a contributory inhibiting one.

In conjunction with the results of other investigations [17] [18] [20], our findings show that the studied hindered amines are capable of entering into a large number of reactions that inhibit photo-oxidation in various ways. There is a great deal of evidence that this multifunctional reactivity is an important characteristic of these highly-active substances.

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Experimental Part

Substances. 4-Benzoyloxy-2,2,6,6-tetramethylpiperidine (**1**) and 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (**2**) were synthesized in our laboratories. Dibenzyl ketone (**3**) was supplied by *Fluka AG* and recrystallized from benzene. The benzene and toluene solvents used were of analytical reagent standard *(Merck AG).*

The products **8** and **9** isolated from the reaction between the nitroxyl **2** and the radicals arising in the photolysis of DBK under N_2 were characterized by means of spectroscopic and elementary analysis.

4-Benzoyloxy-1-benzyloxy-2,2,6,6-tetramethylpiperidine (**8**), m.p. 76-77°. - IR. (KBr): 1706, 1600, 1580, 1493, 736, 711, 690. - ^{1}H-NMR. (100 MHz, $CDCl_3$): 8.04 (*m*, H-C(2',6')); 7.2-7.6 (*m*, H-C(3',4',5')); 7.33 (*m*, benzylic H); 5.30 (*m*, H-C(4)); 4.85 (*s*, OCH_2); 2.04 ($d \times d$, $J = 12$ and 4, H_{eq}-C(3,5)); 1.77 (*t*, $J = 12$, H_{ax}-C(3,5)); 1.35 (*s*, CH_3). - MS.: 367 (1, M^+), 276 (36), 246 (5), 154 (39), 124 (100), 109 (52), 105 (97), 91 (48), 77 (50).

$C_{23}H_{28}O_3N$ (366.5) Calc. C 75.38 H 7.70 N 3.82% Found C 75.5 H 8.1 N 3.9%

4-Benzoyloxy-2,2,6,6-tetramethyl-1-phenylacetoxy-piperidine (**9**), m.p. 104-106°. - IR. (KBr): 1748, 1709, 1592, 1582, 1493, 738, 713, 699. - ^{1}H-NMR. (100 MHz, $CDCl_3$): 8.03 (*m*, H-C(2',6')); 7.2-7.7 (*m*, H-C(3',4',5')); 7.33 (*m*, benzylic H); 5.30 (*m*, H-C(4)); 3.78 (*s*, CH_2CO); 1.7-2.2 (*m*, H-C(3.5)); 1.24 and 1.08 (2*s*, CH_3). - MS.: 395 (1, M^+), 380 (2), 277 (25), 262 (20), 258 (5), 246 (10), 140 (55), 124 (100), 105 (50), 91 (52), 77 (36).

$C_{24}H_{29}O_4N$ (393.5) Calc. C 72.89 H 7.39 N 3.54% Found C 73.2 H 7.4 N 3.4%

Irradiations and determination of the rate of radical formation. Preliminary to the actual experiments, the rate of radical formation was determined in 2 ways. Two 1 cm quartz cells were irradiated side by side by the beam from a 200 W high-pressure Hg lamp rendered parallel by passing through a lens. Before reaching the cells, the beam also passed through an interference filter of 313 nm wavelength. One of the cells served as reference for determining the rate of radical formation in the presence of **2** under N_2, while in the other DBK photolysis occurred in an O_2 atmosphere, the loss of ketone being measured by gas chromatography. To ensure gas saturation, both the N_2 and O_2 were passed through the cells not only during the reaction but also for the previous 30 min. The rate of radical formation during DBK photolysis under N_2 was obtained from the decrease in the concentration of the nitroxyl **2** added as scavenger. The results from the 2 cells agreed surprisingly well (±5%), showing DBK loss is equivalent to the radical formation^3). The actual experiments were carried out under the same conditions as the method described above for radical determination under oxygen.

Analytical. The products formed in the course of DBK photo-oxidation: benzaldehyde (**4**), phenylacetic acid (**5**), benzoic acid (**6**) and benzyl aclohol (**7**) were identified by GC., TLC. and MS. using for comparison authentic samples of analytical reagent standard purchased from *Fluka AG.* Concentrations of reactants and products were measured by GC.: *Varian* 2740, FID, column OV 101, 10%, ¼", 2 m, integrator *Varian* 485.

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^{3}) This means that cage processes and quenching effects of $>$NO· or O_2 play only a subordinate role when DBK is irradiated, a finding that may be connected with the short-lived triplet state of DBK [33].

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