quencher(s) could be formed in the solution as a consequence of the initial photochemical process.

Although it is difficult to rigorously exclude all impurities from the system, impurities probably are not responsible for the observed results because a solvent impurity would not show a dependence on the amount of light absorbed; nitrobenzene and solvents purchased from several sources gave duplicate results, and these results agree with Hurley and Testa's published results at long irradiation times.[3] Thus, the quencher idea is most plausible.

If a quencher is being generated which is not photochemically active, its concentration should be proportional to the total amount of light, and plots of I^0/I vs. E should be linear. Actually, these plots are reasonably linear in the initial stages of the reaction but progressively decrease to zero slope. Thus, the newly formed quencher is also decomposed by light, and its concentration becomes constant after a period of time. Nitrobenzene, itself, is not a quencher since the quantum yields are not dependent on the initial nitrobenzene concentration.

A nitroxide radical(s) is a good candidate for the quencher formed since these are known to be formed under the reaction conditions[13,16,17] and di-*tert*-butyl nitroxide has been used as a triplet quencher.[18] Since nitroxides are destroyed by acid,[16] the 2-propanol–nitrobenzene irradiation was done in an aqueous, acidic solution and the results compared to those from the corresponding neutral, aqueous solution. In acid, the quantum yield remains constant with time, albeit at a lesser value than the initial quantum yield in neutral solution.

The quantum yield effect described herein means that nitrobenzene is more efficient at product formation than earlier recognized. Consequently it is necessary to reevaluate the conclusion of Hurley and Testa[3] that the low quantum yield of nitrobenzene disappearance is due to a short lifetime of triplet nitrobenzene, ca. 10^{-9} s. Their determination was done with the assumption that no complexes are formed between any of the species present. However, nitrobenzene is known to form charge transfer complxes with benzene[19] and piperylene[20] and, furthermore, the formation of such complexes can increase the rates of radiationless processes.

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Registry No.—1,3,5-Trinitrobenzene, 99-35-4; nitrobenzene, 98-95-3; 1-propanol, 71-23-8; 2-propanol, 67-63-0; propanol, 123-38-6; acetone, 67-64-1.

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Ylide Autoxidation during the Stevens Rearrangement

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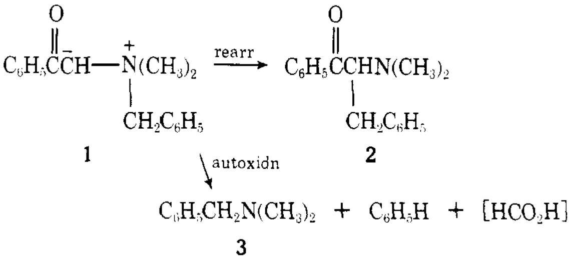
The autoxidation of enolate anions has been studied in detail by Doering and Haines[1] and more recently reinvestigated by Sawaki and Ogata.[2] Although the mechanistic question of a 1,2-dioxetane or an α-keto hydroperoxide intermediate remains unresolved, the overall process of oxidation followed by cleavage is well established.

Carbonyl stabilized ylides provide an example of a special enolate anion in which the onium atom can also participate in the anion stabilization process. Because of our interest in ylide rearrangements[4] it was of concern to know if a similar autoxidation process might occur with these anions. In the following we report our observations that such autoxidation of an ylide does occur competitive with the Stevens rearrangement process at lower temperatures and in those cases when oxygen is present.

Results and Discussion

Ylide **1** smoothly rearranges in chloroform to **2** with a specific rate constant of 5.9×10^{-4} min^{-1} at 0 °C as determined by following the reaction by NMR. The spectral data along with subsequent workup of the reaction mixture showed that dimethylbenzylamine (**3**) was also formed. The ratio of Stevens rearrangement product (**2**) to dimethylbenzylamine (**3**) varied markedly, dependent upon the amount of oxygen present in the reaction mixture (Table I). In addition, the major nonbasic product recovered was benzoic acid in a molar amount similar to the dimethylbenzylamine.



$$\underset{\mathbf{1}}{C_6H_5\overset{O}{\overset{\|}{C}}\bar{C}H-\overset{+}{N}(CH_3)_2 \atop \quad\quad\quad | \; CH_2C_6H_5} \xrightarrow{\text{rearr}} \underset{\mathbf{2}}{C_6H_5\overset{O}{\overset{\|}{C}}CHN(CH_3)_2 \atop \quad | \; CH_2C_6H_5} \qquad (1)$$

$$\mathbf{1} \xrightarrow{\text{autoxidn}} \underset{\mathbf{3}}{C_6H_5CH_2N(CH_3)_2} + C_6H_5H + [HCO_2H]$$

The presence of both dimethylbenzylamine and benzoic acid was of particular interest because of their relationship

Table I. The Effect of Oxygen on Product Distribution[a]

	Rel % products	
Atmosphere	Rearr (2)	Autoxidn (3)
Vacuum[b]	100	0
N_2[c]	76	24
Air[c]	65	35
O_2[c]	37	63
O_2[d]	22	78

[a] Ylide in $CDCl_3$ (0.25 M) at 0 °C. [b] Evacuated and freeze–thaw degassed. [c] Atmosphere over reaction solution. [d] Sample stirred in oxygen atmosphere.

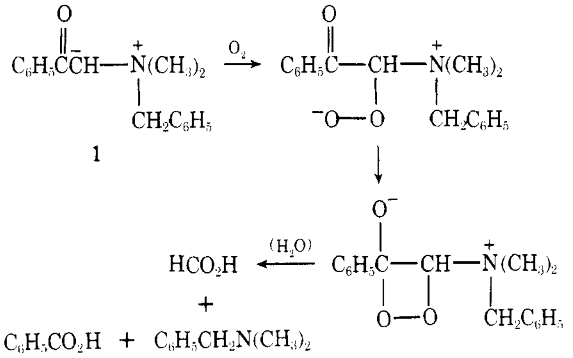
Table II. The Effect of Temperature on Product Distribution[a]

Temp, °C	Rel % products	
	Rearr (2)	Autoxidn (3)
0	65	35
12	75	25
24	86	14
29	88	12
34	91	9

[a] Ylide in $CDCl_3$ (0.24 M) with air atmosphere.

to other potential reaction pathways for the nitrogen ylide. Thus a carbenoid decomposition of the ylide to give tribenzoylcyclopropane and benzyldimethylamine could have been indicated. This process has been observed for phenacyl sulfur[5a] and nitrogen[5b] ylides. However, in our work no tribenzoylcyclopropane (or precursor dibenzoylethylene) was detected. Benzoic acid might have originated through oxidation of the benzyl radical[6] escaping from the proposed radical pair cage of the Stevens rearrangement.[7] Yet no indication of dimethylphenacylamine, the other component of the cage pair, was found.

The phenacyl stabilized ylide is a special case of an enolate anion. Doering and Haines[1] have shown that enolate anions autoxidize and cleave. In the case of phenones, benzoic acid is one of the fragmentation products. In our work, equal amounts of benzoic acid and benzyldimethylamine would be expected to form as is experimentally observed (eq 2). We have also observed the formation of phenyl substituted dimethylbenzylamines when the starting ylides were p-methoxybenzyl and p-chlorobenzyl phenacylammonium.



$$C_6H_5C(=O)\bar{C}H-\overset{+}{N}(CH_3)_2(CH_2C_6H_5) \xrightarrow{O_2} C_6H_5C(=O)-CH(O-O^-)-\overset{+}{N}(CH_3)_2(CH_2C_6H_5) \longrightarrow C_6H_5C(O^-)(-O-O-)CH-\overset{+}{N}(CH_3)_2(CH_2C_6H_5) \xrightarrow{(H_2O)} HCO_2H + C_6H_5CO_2H + C_6H_5CH_2N(CH_3)_2 \quad (2)$$

It is of interest that dimethylbenzylamine was not reported in the many previous studies of the Stevens rearrangement.[7,8] Further results (Table II) demonstrate that there is a marked temperature dependence on the rates of the competitive Stevens rearrangement and autoxidation–cleavage reactions. The latter process is only important at low temperatures. The Stevens rearrangement has normally been studied at elevated temperatures precluding the observation of significant autoxidation product.

Experimental Section

Benzyldimethylammonium phenacyl ylide (1) was prepared by the method of Ollis et al.:[8c] mp 72–73 °C; NMR ($CDCl_3$) δ 3.3 (s, 6), 5.9 (s, 2), 7.3–8.0 (m, 10). (The ylide carbanion proton is not observed.)

Kinetics of the rearrangement process were obtained by mixing the precooled ylide and solvent in a cold NMR tube, then following the disappearance of the ylide $-N^+(CH_3)_2$ peak and appearance of the product $N(CH_3)_2$ peak. The temperature of the reaction was controlled by an appropriate constant temperature bath or by the variable temperature unit of the NMR spectrometer (Varian A-60).

Product analysis was based upon the NMR spectrum of the total reaction, or in some cases by running an identical reaction on a larger scale and isolating products. Final analysis was by gas chromatography and/or NMR spectra.

The effect of oxygen was studied by changing the gas over the sample in the NMR tube or within the flask in larger scale reactions. In one case, the NMR tube was evacuated, sealed, and degassed.

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Registry No.—**1,** 25241-18-3; **2,** 30669-80-8; **3,** 103-83-3.

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A One-Step Conversion of RCH_2CO_2H to $RCH{=}O$

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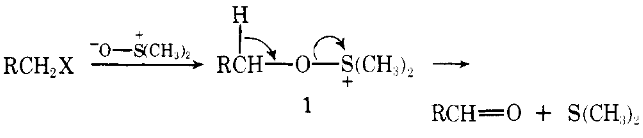
The electrolytic decarboxylation of carboxyl functions to a variety of products has been the subject of much study in recent years.[1] Typically the products are those formed via radical intermediates; however, in some cases the oxidation of the radical to form carbonium ion proceeds more rapidly than the radical reactions.[2,3] Our interest in exploring this area was due to the possibility of utilizing carbonium ions so generated for the production of Moffatt oxidation intermediates. The Moffatt oxidation usually involves[4] solvolysis of alkyl halides or tosylates in dimethyl sulfoxide to form the product 1, which, on treatment with base, decomposes as shown, to an aldehyde and dimethyl sulfide. We have now demonstrated that it is possible to combine the two processes described above by carrying out electrolytic decarboxylation in dimethyl sulfoxide as the solvent to produce directly the Moffatt intermediate. Workup with base according to the usual Moffatt procedure then affords the desired aldehyde.



$$RCH_2X \xrightarrow{^-O-\overset{+}{S}(CH_3)_2} R\underset{H}{C}H-O-\overset{+}{S}(CH_3)_2 \longrightarrow RCH{=}O + S(CH_3)_2$$

$$RCH_2CO_2H \xrightarrow[-CO_2]{-e} [RCH_2{}^+] \xrightarrow[2.\ \text{base}]{1.\ Me_2SO} RCH{=}O$$

This reaction was run on a number of phenylacetic acids. The results of this survey are summarized in Table I. It is apparent from the failure of 4-nitrophenylacetic acid to undergo this transformation that the reaction indeed does involve a carbonium ion and is not a free-radical process.

Experimental Section

Electrolysis Apparatus. The electrolytic vessel was a 100-ml three-neck round-bottom flask fitted with a Claisen adapter con-