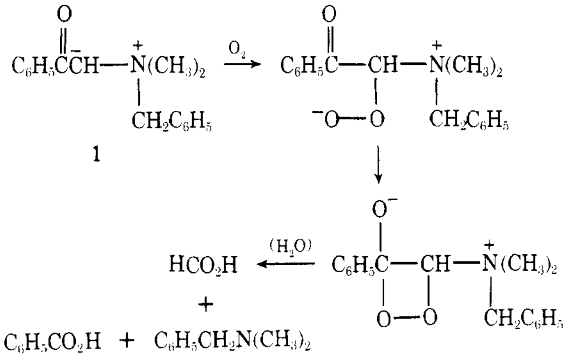
Table II. The Effect of Temperature on Product Distribution[a]

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.



(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.

Acknowledgment. Support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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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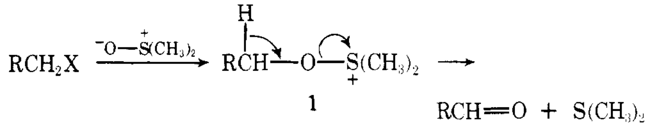
Received July 2, 1976

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.



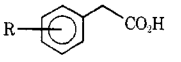
$$RCH_2CO_2H \xrightarrow[-CO_2]{-e} [RCH_2{}^+] \xrightarrow[\text{2. base}]{\text{1. }Me_2SO} RCH{=}O$$

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-

Table I. Oxidative Decarboxylation of Phenylacetic Acids

 R = [a]	Aldehyde, %[b]	Kolbe dimer, %[c]	Other products, %[d]
4-Methoxy	72		4-Methoxybenzoic acid, 14%
3-Methoxy	78		3-Methoxybenzoic acid, 12%
4-Chloro	62	12	4-Chlororbenzoic acid, 15%
Hydrogen	41	52	
4-Nitro	0	82	

[a] Registry no. are, respectively, 104-01-8, 1798-09-0, 1878-66-6, 103-82-2, 104-03-0. [b] Registry no. are, respectively, 123-11-5, 591-31-1, 104-88-1, 100-52-7. [c] Registry no. are, respectively, 5216-35-3, 103-29-7, 736-30-1. [d] Registry no. are, respectively, 100-09-4, 586-38-9, 74-11-3.

taining a gas lead in pipe and condenser, and, in the outer joints, a pair of smooth platinum electrodes (1 cm^2). The electrodes were placed parallel to each other 3 cm apart.

4-Methoxybenzaldehyde. To a solution of 3.32 g (0.02 mol) of 4-methoxyphenylacetic acid in 70 ml of dry Me_2SO was added 0.48 g (0.01 mol) of 50% sodium hydride suspended in mineral oil. This solution was placed in the above cell. The solution was degassed by bubbling nitrogen through the stirred solution for 30 min. Fifty-five volts at 0.25 A was applied to the solution for 4 h. Sodium bicarbonate (5 g, 0.065 mol) was added and the mixture heated to 150 °C for 4 min and cooled rapidly by quenching in an ice bath. The mixture was poured into 350 ml of saturated sodium chloride solution. This was extracted with 4 × 150 ml of ether. Evaporation of the solvent left an oily residue which, on distillation, afforded 1.96 g (74%) of 4-methoxybenzaldehyde. The physical and spectral properties were identical with those of an authentic sample.

The aqueous layer was acidified and extracted with 3 × 75 ml of ether. On evaporation of the solvent a crystalline solid remained which was recrystallized to afford 0.44 g (14%) of 4-methoxybenzoic acid.

The reaction was repeated with the following phenylacetic acids: 3-methoxy, 4-chloro, hydrogen, and 4-nitro. The results are given in Table I. All products were identified by comparison with authentic samples.

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Preparation of Alkyl Phenyl Sulfides by Electrophilically Catalyzed Displacement of Certain Nucleophiles by Thiophenoxy Group[1]

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Received November 3, 1976

Water and alcohols are commonly considered to be solvents of high nucleophilicity[2] and upon their reaction with a carbenium ion afford the corresponding alcohol and ether. In fact, Winstein et al.[3] have employed water as an effective agent for intercepting carbocationic species in order to elucidate relevant reaction mechanisms. More recently certain charged nucleophiles, such as azide ion, have been used for the same purpose.[4] Comparing Ritchie's N_+ values for various *charged* nucleophiles, it appears that thiophenoxide anion is by far a better trapping agent than azide by over two orders of magnitude in methanol and even larger in Me_2SO.[4] N_+ values for a given nucleophile show a marked dependence upon the medium, the obvious trend being the greater the basicity of the medium the larger the N_+ value. In a protic medium of high acidity thiophenoxide can no longer exist, of course, as a charged species but rather as its protonated form, namely thiophenol. The purpose of this note is to show that thiophenol itself exhibits a marked reactivity toward carbenium ions, being capable of displacing rather readily various nucleophiles at a carbenium ion center (eq 1).

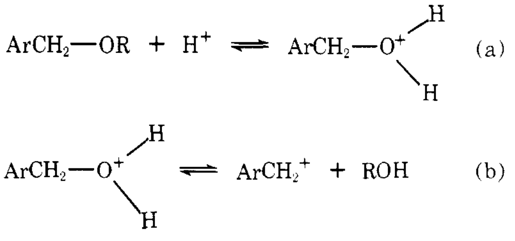
$$RZ + PhSH \xrightarrow{\text{cat.}} RSPh + HZ \qquad (1)$$
$$Z = OH, OR, Cl, N_3$$

The ready conversion of triphenylcarbinol and *tert*-butyl alcohol to the corresponding alkyl sulfides by their acid-catalyzed reaction with thiols[5] has been known for a long time. It is quite probable that this reaction owes its feasibility to the ready ionization of these alcohols in acid media, and to the pronounced nucleophilicity of thiols. Employing a modification of this method we found that certain alkyl phenyl sulfides can be prepared very conveniently and in high yields. The results are summarized in Table I. According to this method an alcohol is transformed to the corresponding alkyl phenyl sulfide by boiling an equimolar mixture of the alcohol and thiophenol in benzene or methylcyclohexane, in the presence of perchloric acid catalyst. The results indicate that ease of reaction and product yield are highly dependent on the structure of the alcohol. Aryl methanols and tertiary alcohols, which are expected to have high pK_{R^+} values, react readily with thiophenol and the yields of the sulfides are usually good to excellent. Primary alcohols require exceedingly long reaction times and even so the corresponding sulfides are produced in very poor yields.

Perhaps more novel could be the ready displacement of alcohol in the acid-catalyzed reaction between thiophenol and certain ethers. Upon dissolving an equimolar mixture of 2-phenylisopropyl methyl ether and thiophenol in trifluoroacetic acid (TFA) an exothermic reaction takes place and the ether is transformed instantly into the relevant phenyl sulfide (eq 2).

$$Ph(CH_3)_2COCH_3 + PhSH \xrightarrow{\text{TFA}} Ph(CH_3)_2CSPh + CH_3OH \qquad (2)$$

Results with various ethers from reactions such as 2 are summarized in Table II. Two main factors seem to emerge from the examination of the data. (a) The basicity of the ether; comparing cases 2 and 3 it can be seen that methyl ether is less reactive than the ethyl analogue, and this might well be due to lower basicity of the methyl ether[6] (eq 3a). (b) The stability



$$ArCH_2{-}OR + H^+ \rightleftharpoons ArCH_2{-}O^+(H)H \qquad (a)$$
$$ArCH_2{-}O^+(H)R \rightleftharpoons ArCH_2^+ + ROH \qquad (b)$$

(3)

of the carbenium ion produced in step b obviously is the second important factor. *o*-Chlorobenzyl methyl ether appears to be inert under the reaction conditions employed in this investigation, whereas the *p*-chlorobenzyl ether reacted incompletely. This can be understood by comparing, for example, the ionization potentials of benzyl and *p*-chlorobenzyl radicals.[8] *p*-Chlorobenzyl cation appears to be less stable by