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Autoxidation of Diphenylketene. 1. Conditions and Products

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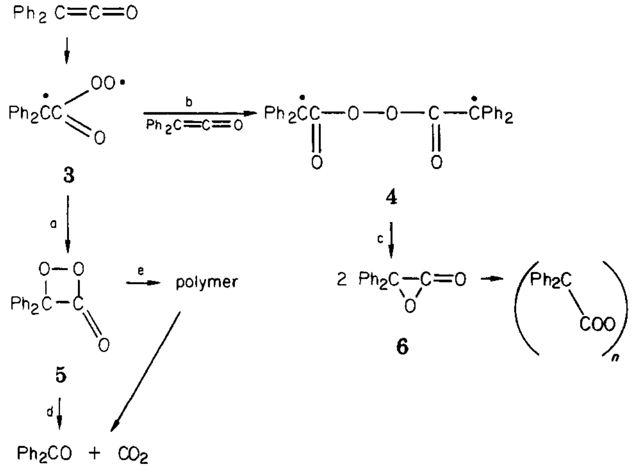
In addition to the main product, polybenzilic acid, and benzophenone, the autoxidation of diphenylketene in carbon tetrachloride has been shown to lead to phenyl benzoate (9–27%). The precursor of polybenzilic acid is diphenylacetolactone, which has been trapped by hexa- and pentafluoroacetone included in the autoxidation solution. Under appropriate conditions trace diphenylacetolactone can also be trapped by diphenylketene itself, leading to the product **9**. The mechanism of the autoxidation is discussed in the light of the new observations. The detailed kinetics is still under investigation and will be reported subsequently.

Introduction

The ketenes exemplify not only the high reactivity of a cumulenic double bond but the dependence of its behavior on substituents.[1,2] Whereas aldoketenes do not autoxidize readily, dimethylketene reacts spontaneously with oxygen to yield a peroxy lactone polymer, stable at −10 °C; the corresponding peroxy polymer in the case of diphenylketene, inferred from the cleavage to benzophenone and carbon dioxide, is a minor product, the major one being the polymer of an α-lactone.[2-5]

Recently the chemistry of strained oxygen-containing rings such as those related to these reactions has made rapid progress. α-Lactones have been shown to be chemical intermediates in a number of cleavage and oxidation reactions.[6-17] α-Peroxy lactones, too, have been synthesized and their chemical reactivity and luminescent behavior have been studied.[18-21] In addition, there has been rapid development in the related field of dioxetane chemistry.[22]

Scheme I



The demonstrated reality of these reactive intermediates lends added interest to the attempt to work out the actual reaction paths by which ketenes are converted into the

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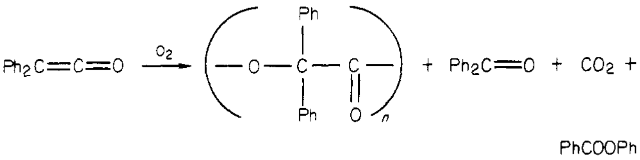
Table I. Benzophenone and Phenyl Benzoate from Autoxidation of Diphenylketene (DPK)

run	conditions	Δ DPK, mmol	% benzophenone	% phenyl benzoate
15	CCl_4, 0 °C	2.9	25	16
16	CCl_4, 0 °C	0.45	35	22
24	CCl_4, air, 0 °C	3.2	23	13
25	CCl_4, 0 °C	3.4	21	16
20	CCl_4, 25 °C, 40 lb of O_2	2.9	17	12
21	CCl_4, 25 °C, 40 lb of O_2	3.1	18	10
28	CCl_4, 25 °C, 40 lb of air	3.2	14	9
32	CCl_4, 25 °C, 2100 lb of O_2	5.1	16	14
27	CCl_4, 40 °C, 1 atm of O_2	3.6	20	14
29	$CCl_4/CHBr_3$ 9:1, 0 °C	3.8	34	8
30	$CHBr_3$, 10 °C, 1 atm of O_2	3.5	48	0

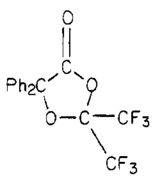
observed products in an autoxidation reaction without any recognized initiator.

Results

Products of Diphenylketene Autoxidation. The major product of the autoxidation of diphenylketene is the polyester of benzilic acid,[6] of variable degree of polymerization up to about 14,[23] corresponding to oxene oxidation of the ketene. This polyester is known to be formed



rapidly by polymerization of diphenylacetolactone[10] (**6**, Scheme I); that the lactone is indeed the precursor of the polymer in diphenylketene autoxidation was shown by performing the oxidation at −78 °C in the presence of hexafluoro- or pentafluoroacetone. The trapping products, **1** and **2** were isolated in yields of 1.4% and 15.4%, respectively.



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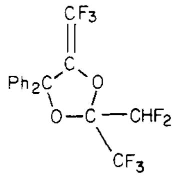


2

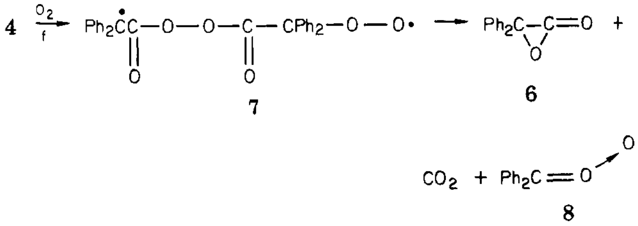
spectively. Both products showed carbonyl stretching bands in the infrared at 1830 cm^{-1}, and **2** had a characteristic ^{1}H NMR triplet at 5.95 ppm (J = 52 Hz).

The polyester has IR and NMR spectra indicative of a uniform structure (unconjugated ester groups, aromatic rings, and two kinds of nonaromatic carbons at 164.7 and 87.6 ppm) with no indication of any end-group structures. In a number of autoxidation runs the polyester was isolated as a white powder, after completion of the oxygen absorption, by precipitation with pentane, cooling, and filtration. Elemental analysis of such samples showed the correct composition for the polyester. Yields of the polyester based on diphenylketene were between 51% and 71% in a series of nine runs in carbon tetrachloride solvent, being as low as 20% only in bromoform (see below).

Although no other cyclic products of the autoxidation were identified, there was a component which, on warming to 50 °C in the presence of perylene, gave rise to luminescence (see Experimental Section).

Separation of the nonpolymeric products by vapor chromatography revealed not only the benzophenone (16% to 31%) previously recognized in such autoxidations but amounts of phenyl benzoate from 12% to 18%. Again bromoform yielded a quite different product composition, with no phenyl benzoate and a production of benzophenone amounting to 48%. The total material balances in carbon tetrachloride averaged 94% but ran as low as 77% where complete absorption of oxygen was not attained. Table I shows the yields of benzophenone and phenyl benzoate in eleven runs.

Scheme II



7 **6** **8**

Diphenylketene is known[10] to be convertible into the α-lactone by the action of ozone. A workup of the product of such a reaction yielded the same three principal products seen in the autoxidation but with a greater amount (83.4%) of the polyester along with 14.5% of benzophenone and 2.1% of phenyl benzoate. These figures are appropriate for competition of direct ozonation of diphenylketene with its autoxidation.

The products of autoxidation of diphenylketene present a number of mechanistic problems; a complete understanding of how these products are formed would carry with it answers to some longstanding questions. Does benzophenone arise from cleavage of an initially formed peroxy lactone? If so, the benzophenone may owe its occurrence entirely to 1:1 processes involving intersystem crossing[3] and not to cleavage of an alternating copolymer of the ketene and oxygen, as in the classical model of styrene oxidative cleavage.[24] In that model, cleavage to carbonyl compounds occurs together with formation of epoxide, analogous to the α-lactone in the present case, and all by way of free radical chains. An important difference between the two cases is the formation of the α-lactone here as the major product, something which is not possible by the unmodified Mayo chain mechanism.

It may well be that the minor proportions in which epoxide occurs in the autoxidation of sytrene are the joint result of two specific properties of the styrene autoxidation: the related facts that it is initiated and carried by monoradicals, and that the kinetic chains are long. Chain reactions involving *biradicals* are less well-documented, yet with such chains termination should become much easier and chains accordingly much shorter. Moreover, it is hard to imagine a substrate more likely to enter into biradical

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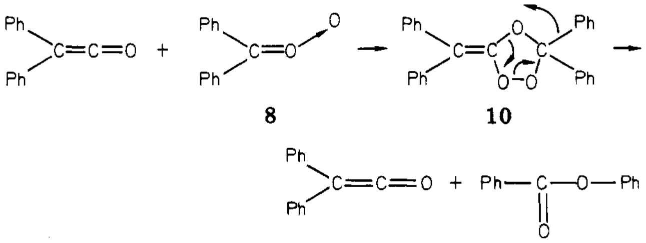
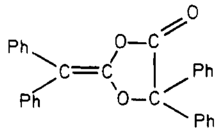
Scheme III



chains than diphenylketene. Thus, it seems well to consider the possibility that the two modes of oxidation—leading to α-lactone and to peroxy lactone—arise in as simple a way as $3 \rightarrow 5 \rightarrow$ benzophenone or $3 \rightarrow 4 \rightarrow 6$ (Scheme I). One may ask whether 4 should be completely impervious to attack by oxygen; it is interesting that if some O_2 did add to 4, the expected result would be 7 cleaving to $6 + CO_2 + 8$ (Scheme II). The carbonyl oxide 8,[25,26] in the absence of a reactive trap, might well rearrange to phenyl benzoate. This rearrangement, the direct cleavage of the peroxy lactone, and the polymerization of the α- lactone, are all nonradical processes, yet the intermediates 5, 6, and 8, which undergo these diverse reactions, could all be initially formed in the connected biradical process indicated.

The isolation of another new compound has a bearing on the possible interception of reactive intermediates in the autoxidation process. After the distillation of some diphenylketene, the pot residue was investigated by column chromatography and 500 mg of colorless crystals, mp 113.5–114.5 °C, were isolated which proved to have the structure 9 by X-ray crystallography,[27] supported by appropriate mass spectrum, IR, and ^{13}C and ^{1}H NMR. This trapping product of the α-lactone by diphenylketene was never seen among the products of an autoxidation run, which indicates that the polymerization of the α-lactone (believed to exist in its dipolar ion form[10]) is faster than any competing reaction. However, the distillation of diphenylketene involves temperatures where the polyester is no longer stable, and under these conditions formation of 9 is the favored reaction of the liberated lactone 6. Alternatively, the traces of oxygen responsible for the oxidation in this case may have produced the lactone at such a low concentration that its polymerization could not compete with addition t the ketene. The isolation of 9 is just one example of the presence of adventitious oxidation products in diphenylketene from which reasonable attempts had been made to exclude oxygen.



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In view of this demonstration that diphenylketene can scavenge 1,3-dipolar reagents, the ketene might well act to hasten the rearrangement of benzophenone oxide 8 to phenyl benzoate (Scheme III).

Rates of Reaction. We have made exploratory rate measurements in a total of eight solvents, in closed systems over a range of pressures and in other cases under continuous bubbling of oxygen. The reproducibility of the results depends critically upon the technique of purification, oxygen handling, and analysis. Some of these points are still undergoing refinement and will be reported in part 2 of this work. At this point we shall discuss only certain established characteristics which are directly related to the mechanism.

The most familiar polymerizations and autoxidations of olefinic compounds proceed so much more efficiently under initiation by free-radical-forming agents that they are commonly regarded as requiring such initiators for their occurrence. Nevertheless, even the prototype styrene is capable of slow reactions spontaneously generating free radicals,[28] and such "molecule-assisted homolyses" have been shown to be rather general.[29]

In the present experiments the oxidation was clearly spontaneous, and the variations in rate could not be correlated with acid or base impurities, small changes in moisture content, or stray light intensity.

The preliminary rate studies all agree that the autoxidation is between first and second order in diphenylketene; a fair fit to three-halves-order kinetics could be had in most cases, and these figures were used empirically in making comparisons in overall rate amoung different runs. By this method the reaction seems to be about five times as rapid in acetonitrile as in chloroform. This difference, the greatest seen among the eight solvents investigated, is compatible with mild charge transfer but seems to exclude any strongly ionic character in the initiation reaction.

In nine runs in which the concentrations of benzophenone and phenyl benzoate were followed with time, the buildup of these products showed no clear departure from linearity relative to the diphenylketene consumption throughout the run. Run 30, in bromoform, which yielded no phenyl benzoate, was abnormal in yet another respect: the plot of benzophenone formed vs. ketene consumed became less steep after about 40% reaction, ending with a 42% lesser slope than initially.

These facts place an important limitation on the selection of a mechanism in that they require that the three major products all be formed (in the non-bromoform solvents) with the same kinetic order in reactants. If diphenylacetolactone, benzophenone, and phenyl benzoate are formed from successive intermediates in the autoxidation, then the probability of one intermediate passing into another must not change with the changing concentrations of the reactants.

Some Features of the Mechanism. Some details of the mechanism are best discussed in conjunction with the detailed kinetic study (part 2). However, the observations here reported set some requirements to which the mechanism must conform and allow us to describe the autoxidation of diphenylketene in more detail than has been possible before.

It is helpful to view Schemes I and II in the light of the intersystem crossings which they require in order to run their course. Since the reaction is initiated by ground-state triplet oxygen, the peroxy biradical 3 or its isomeric molecular complex will originate as a triplet. The triplet 3 is free to react with diphenylketene to yield the new triplet biradical 4, but the direct alternative route to benzophenone via 5 will require an intersystem crossing. Intersystem crossing is also required for 4 to cleave to the α-lactone 6. In the case in which the free radical reactions b (Scheme I) and f (Scheme II) are faster than intersystem crossing, 7 will be the first species formed which is singlet and can pass directly to all-singlet products—50% α-lac-

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[25] R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 14, 745 (1975).

[26] R. Criegee and H. Korber, *Ber.*, **104**, 1812 (1971).

[27] W. H. Watson, R. E. McCluney, and V. Zabel, to be published.

[28] See C. Walling, "Free Radicals in Solution," Wiley, New York, 1957, pp 180–184.

[29] W. A. Pryor, "Organic Free Radicals," A. C. S. Symp. Ser., American Chemical Society, Washington, DC, 1978, pp 33–62.

tone polymer and 50% divided between benzophenone and phenyl benzoate according to the most favorable reaction of benzophenone oxide under the circumstances. Intersystem crossing of **3** will lead to increased benzophenone, while intersystem crossing of **4** will boost the polyester content of the product. An obvious possibility for the unique effect of bromoform is that this heavy-atom solvent causes intersystem crossing before there is any formation of **7**, the first possible source of phenyl benzoate in this sequence. It is, of course, also possible that the fate of the peroxy biradical is altered by capture of H from bromoform. This possibility remains to be tested.

Table I shows that in the runs in carbon tetrachloride the ratio of benzophenone to phenyl benzoate formed is constant at 1.50 with a mean deviation of 0.15, whereas the sum fo the two products varies from 23.4% to 56.5%. We note, however, that every product distribution observed can be interpreted in terms of Schemes I and II, with the competition among product-forming steps being influenced by the solvent as well as the reactant concentrations.

Experimental Section

Preparation of Solvents. Chloroform, methylene chloride, and carbon tetrachloride were distilled from P_2O_5. Toluene, benzene, petroleum ether, and hexane were dried over sodium and distilled. Bromoform was dried over anhydrous potassium carbonate and distilled under reduced pressure. Acetonitrile was distilled from calcium hydride under reduced pressure.

Preparations of diphenylacetyl chloride and of diphenylketene were carried out as in "Organic Syntheses".[30]

Autoxidation of Diphenylketene in Hexafluoroacetone. A 100-mL round-bottom flask with side arm was purged with dry oxygen and cooled to −78 °C in a dry ice/acetone bath. A dry ice condenser protected with a drying tube was fitted to the flask. The flask was then charged with 36.1 g (217.5 mmol) of hexafluoroacetone by allowing the gas to condense into the flask through the oxygen inlet. Diphenylketene (1.80 g, 9.27 mmol) was added and the mixture was stirred magnetically. The ketene is fairly insoluble in hexafluoroacetone at low temperature, so 15 mL of methylene chloride was added. Dry oxygen was then bubbled through the solution at low temperature for 6.5 h.

The condenser was allowed to warm up and the excess hexafluoroacetone allowed to escape. The remaining methylene chloride solution was extracted with 30 mL of saturated aqueous sodium bicarbonate to hydrolyze the remaining diphenylketene and remove the resulting diphenylacetic acid. The methylene chloride layer was drawn off, dried with magnesium sulfate, and partially evaporated. This solution was then added dropwise to 200 mL of pentane to precipitate the polyester. The polyester was collected by vacuum filtration, dried under vacuum at room temperature, and weighed, resulting in 0.30 g (1.43 mmol) of polyester or 15.4% yield based on starting ketene.

The aqueous layer from the extraction was acidified with dilute hydrochloric acid and the diphenylacetic acid precipitated. The organic acid was then collected by vacuum filtration, dried under vacuum at room temperature, weighed. The acid (0.41 g, 1.93 mmol, 20.8%) was recovered.

The filtrate from collection of the polyester was then evaporated to dryness leaving 0.85 g of an oil which was shown by infrared spectroscopy to be a mixture of low molecular weight esters, benzophenone, and the adduct (**1**) of hexafluoroacetone with diphenylacetolactone. The adduct (5,5-diphenyl-2,2-bis(trifluoromethyl)-1,3-dioxolan-4-one was identified by its carbonyl IR absorption at 1830 cm^{-1}.

Separation of the mixture was effected by liquid chromatography over silica gel by using a 1:1 mixture of hexane and methylene chloride as eluent. The adduct of interest was eluted first, then the esters, and finally the benzophenone. Only 50 mg of the adduct (M_r = 376) was isolated, corresponding to 0.1 mmol or 1.4% based on ketene consumed by autoxidation. The infrared spectrum of the adduct corresponds identically with that of the adduct isolated by Wheland[10] from the ozonolysis of diphenylketene in hexaflouroacetone at low temperature.

Autoxidation of Diphenylketene in Pentafluoroacetone. Autoxidation of diphenylketene was conducted as in the previous experiment, except with pentafluoroacetone instead of hexafluoroacetone. The flask was charged with 20 g (0.147 mol) of pentafluoroacetone and 3.33 g (17.2 mmol) of diphenylketene and autoxidation was conducted for 2.5 h. After 2.5 h, most of the pentafluoroacetone had escaped and the reaction was stopped. After extraction with aqueous sodium bicarbonate to remove unreacted ketene and precipitation of the polyester from pentane, 1.78 g of a clear oil remained.

The oil was distilled under vacuum yielding 0.95 g (2.65 mmol) of the adduct **2**, bp 106–110 °C (0.5 mm); δ 7.2–7.6 (m, 10 H), 5.95 (t, 1 H, J = 52 Hz). The infrared spectrum was very similar to that of the hexafluoroacetone adduct **1** with a carbonyl stretching frequency of 1830 cm^{-1}. Yield based on ketene consumed by autoxidation was 15.4%.

Ozonolysis of Diphenylketene. In a 250-mL three-necked round-bottomed flask were placed 0.5517 g (2.84 mmol) of diphenylketene and 250 mL of CH_2Cl_2. The solution was cooled to −95 °C with a methanol/liquid nitrogen slush bath while dry nitrogen was passed through the solution. The mixture was then ozonized for 1.25 h at which time all of the ketene color had faded.

The reaction mixture was allowed to warm to room temperature and was analyzed by standard techniques. Yields based on recovered oxidation products were: polyester, 83.4%; benzophenone, 14.5%; and phenyl benzoate, 2.1%.

Chemiluminescence of the Reaction of Diphenylketene with Oxygen. In a 100-mL three-necked round-bottomed flask fitted with a stopper, a calcium chloride drying tube, and a pipette fitted into a thermometer adapter were placed 1.00 g (5.15 mmol) of diphenylketene and 50 mL of CH_2Cl_2. Dry oxygen was bubbled through the pipette and the flask was cooled to 0 °C in an ice bath. After 2 h, two 0.15-mL aliquots of the reaction mixture were removed and placed in two 5-mm quartz ESR tubes, containing 0.15 mL of CH_2Cl_2 and 0.15 mL of 1×10^{-4} M perylene in CH_2Cl_2, respectively. Both tubes and their contents had been precooled to 0 °C.

Each tube, in turn, was placed in the sample chamber of the luminescence apparatus and heated rapidly to 50 °C during which time the light output was recorded as a function of time. The sample without perylene gave no luminescence. However, the sample with the fluorescer perylene showed a luminescence which reached maximum intensity after about 40 s and was still at half its maximum after 2 min.

The same experiment was repeated at −78 °C but no luminescence was obtained.

Determination of Benzophenone and Phenyl Benzoate. Quantities of benzophenone and phenyl benzoate present at any point during a kinetic run were determined by GC with a 1/8 in. × 10 ft stainless steel column packed with 5% SE-30 on Chromsorb W, 60/80 mesh, with diphenylmethane as an internal standard. The separation was performed isothermally at 165 °C. Injector and detector temperatures were 250 °C with a carrier flow rate of 40 mL/min.

Quantitative Determination of the Polyester of Benzilic Acid. The polyester of benzilic acid was isolated at the end of each ketene autoxidation by the procedure previously described by Wheland.[10] After complete disappearance of diphenylketene, the reaction mixture was reduced in volume to between 5 and 10 mL. This was then added dropwise to 200 mL of pentane and the resulting white flocculent polymer filtered off. The white chalky polymer obtained by cooling and filtration was dried under vacuum and weighed.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the National Institutes of Health for support.

Registry No. **1**, 7767-68-2; **2**, 87337-11-9; **6**, 30436-19-2; $Ph_2C{=}C{=}O$, 525-06-4; polybenzilic acid, 49741-69-7; hexafluoroacetone, 684-16-2; pentafluoroacetone, 431-71-0; phenyl benzoate, 93-99-2; benzophenone, 119-61-9.

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[30] E. C. Taylor, A. McKillop, and G. H. Hawks in "Organic Syntheses," H. O. House, Ed., Wiley, New York, Collect Vol. 52, 36 (1972).