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# OXYGEN TRANSFER REACTIONS OF AMINE N-OXIDES—III

## REACTION OF KETONES AND ACID CHLORIDES

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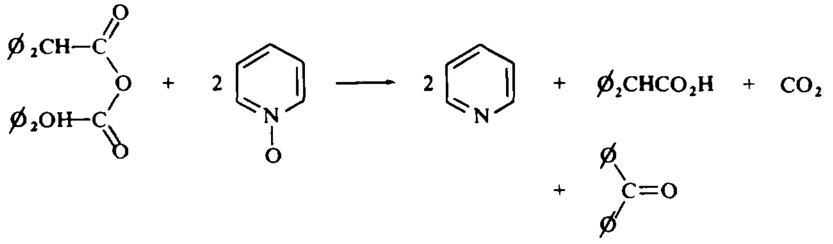
**Abstract**—The products of the reactions amine N-oxides with diphenylketene, diphenylacetyl chloride, biphenyleneketene, 9-fluorencarbonyl chloride and 1,2-diphenyl cyclopropene-3-carbonyl chloride are those expected from the intervention of a highly reactive electrophilic intermediate. Possible structures for this intermediate are discussed.

Amine N-oxides have been found to react with acylating agents to give a rather wide variety of products.[1-4] One of the most recently discovered of these reactions is the oxidative decarboxylation of acyl residues containing active α-H atoms, shown below for diphenylacetic anhydride and pyridine N-oxide.[5-8]

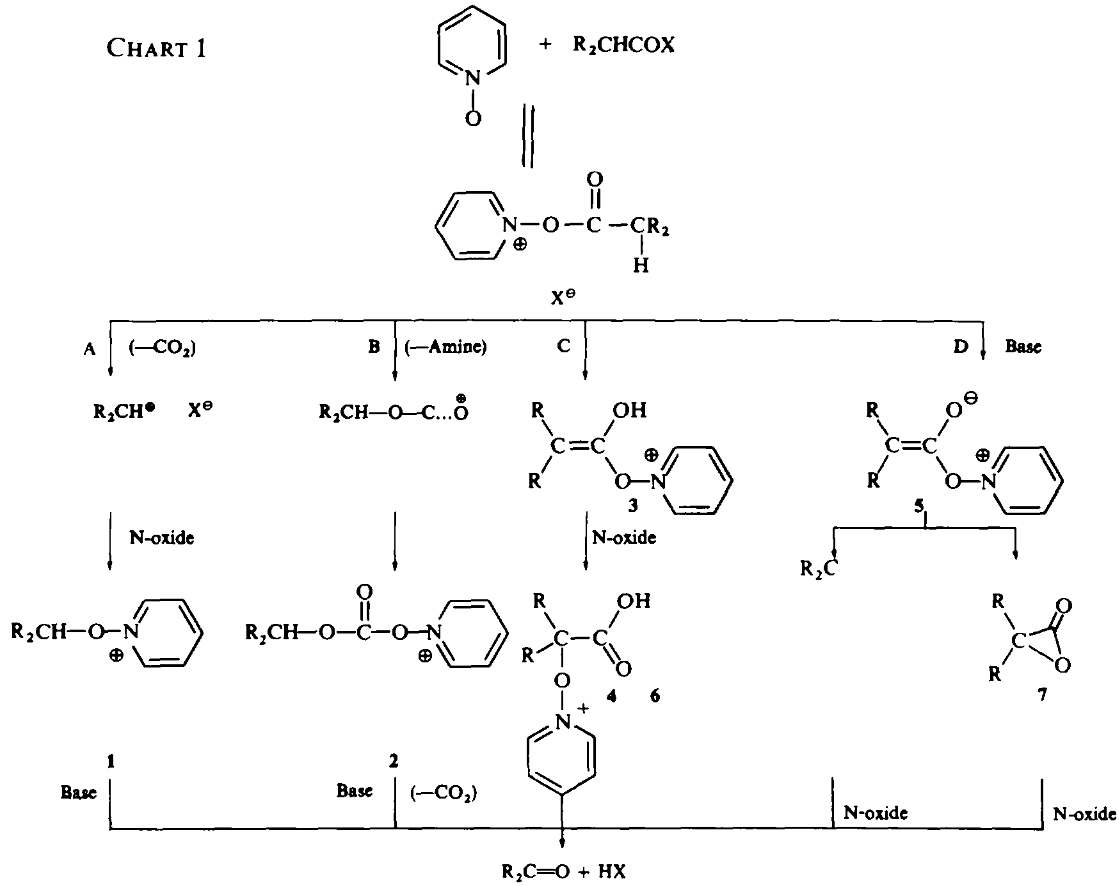


A number of mechanisms have been considered for this overall process. These are summarized in Chart I.

Previous work has made the first two possibilities (A and B) seem unattractive as general mechanisms for this type of process.[7, 8] The results of our own initial investigation of the reaction of 4-picoline N-oxide with phenylacetic anhydride led us to favor mechanism D with the involvement of an "α-lactone like" species (7) as the critical intermediate. The results[6] which led to this suggestion were, the apparent rate law for the reaction which was only first order in N-oxide and inverse first order in carboxylic acid, the deuterium distribution in the products from partially deuterated anhydride and the similarity of products formed from N-oxides and diphenylketene under aprotic conditions. This latter reaction might reasonably be expected to proceed by initial formation of **5** and have subsequent steps in common with the anhydride reaction.

An alternative to D is the enol mechanism (C)[5] which *could* fit the data for the anhydride N-oxide reaction but not the ketene N-oxide reaction since this latter process occurs under conditions where there is no available proton source. The

CHART 1



present report contains the results of our studies of the reaction of N-oxides with ketenes and acid chlorides.

## RESULTS

The reaction of diphenylketene was studied in two ways: by addition of solutions of purified ketene to N-oxide solutions (I), and by *in situ* formation of the ketene from the acid chloride through the action of triethylamine without removal of the triethylammonium chloride (II). Experiments using 4-picoline N-oxide with added pyridine and ethyl vinyl ether were also carried out. The results are summarized in Table 1. The analytical procedures are described in the experimental section.

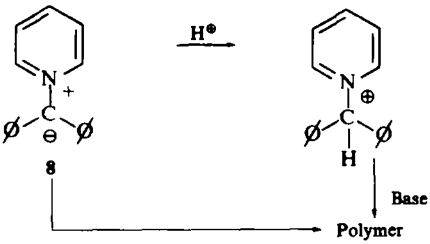
The products obtained from the purified ketene runs at room temperature (I) include reasonably high yields of carbon dioxide. Variation in solvent and temperature had minor effects. The yields of benzophenone were always low by comparison and significant amounts of intractable material were always isolated. Similar material can be isolated by slow addition of diphenylacetic anhydride to hot N-oxide solutions. The amount of this material isolated from the ketene reaction carried out in the presence of triethylammonium chloride was reduced. Instead, N-benzhydrylpicolinium and pyridinium salts were isolated from these runs. These salts were also

TABLE. 1. KETENE—N-OXIDE REACTION PRODUCTS

| N-Oxide | Ketene | Ratio[a] | Temp. | Solvent | $CO_2$[h] | Ketone[h] | Other[h] |
|---|---|---|---|---|---|---|---|
| Pyr. (0·5M) | Diphenyl[b] | 3 | Reflux | Benzene | 0·70 | 0·46 | Polymer |
| Pyr. (0·8M) | Diphenyl[b] | 4 | R.T. | Benzene | 0·46 | 0·46 | Polymer |
| Pyr. (0·7M) | Diphenyl[b] | 2 | Reflux | Acetonitrile | 0·63 | 0·46 | Polymer |
| 4-Pic. (1·4M) | Diphenyl[b] | 4 | Reflux | Acetonitrile | 0·84 | 0·48 | Polymer |
| 4-Pic (1·4M) | Diphenyl[b] | 2 | R.T. | Acetonitrile[f] | 0·60 | 0·50 | Polymer |
| 4-Pic. (1·2M) | Diphenyl[d] | 1 | R.T. | Acetonitrile | 0·15[e] | 0·25 | 0·35 Pic. Salt |
| Pyr. (1·9M) | Diphenyl[d] | 2 | R.T. | Acetonitrile | 0·82 | 0·36 | 0·19 Pic. Salt |
| 4-Pic. (0·6)[c] | Diphenyl[d] | 3 | R.T. | Acetonitrile | 0·23[e] | 0·34 | 0·05 Pic. Salt,<br>0·20 Pyr. Salt |
| 4-Pic (0·4) | Fluorenyl[b] | 8 | R.T. | Acetonitrile | 0·61 | 0·31 | g |
| 4-Pic. (0·7) | Fluorenyl[b] | 6 | R.T. | Acetonitrile | 0·67 | 0·45 | g |

[a] Ratio of initial N-oxide to ketene starting materials. [b] Purified ketene. [c] 1 Equivalent of pyridine added initially. [d] Ketene generated *in situ* from the acid chloride and triethylamine. [e] Determined by volume evolved gases, a procedure which was subsequently found to be unreliable. [f] 10% Ethyl vinyl ether present and not incorporated in products. [g] *Bis*-biphenylene succinic anhydride. [h] Moles/mole ketene.

found to give intractable material when subjected to strong base. Thus, the common presence of ylide **8** is suggested.



When pyridine was present initially under condition II, both picolinium and pyridinium salts were isolated. The relative yields depended on the relative amounts of pyridine to 4-picoline N-oxide which were initially present. Control experiments demonstrated that pyridine does not react with benzhydryl chloride rapidly enough to account for the salt so that some other intermediate such as **4**, **6**, or **7** seems to be needed.

The reaction of biphenylene ketene was also examined under condition I. The results, also included in Table 2, were similar except that the ylide corresponding to **8** was observed directly as a product[9] and the polymer formation was reduced. In addition, a new product was isolated and identified as bis-biphenylenesuccinic anhydride. This material was apparently also isolated from the autoxidation of the same ketene by Staudinger[10] in 1905. Its structure was determined by independent synthesis.

The same formal reactions were also found to occur under a third set of conditions (III) using the corresponding acid chlorides. In the diphenylacetyl case, addition of an acetonitrile solution of the N-oxide to a cold solution of the acid chloride gave an immediate yellow color and only slow evolution of carbon dioxide. Infrared spectra of these solutions showed carbonyl adsorption at 1830 $\text{cm}^{-1}$ and no lower frequency carbonyl bands. This suggests complete formation of the N-acetoxonium chloride salt.[11] Subsequent treatment of these solutions with triethyl amine produced rapid gas evolution and products similar to those observed from the ketene under condition II. When pyridine was added, the reaction was slower but the products were similar. These data are summarized in Table 2.

The yield of ketone, in these runs, shows a clearly defined increase with increasing N-oxide concentration while the yields of the pyridinium salts decrease. The reaction of fluorene-9-carbonyl chloride required no catalyst and proceeded rapidly upon addition of the acid chloride to the N-oxide. The products were again similar to those observed from the corresponding ketene. The reaction of 2,3-diphenylcyclopropene-1-carbonyl chloride was also examined under these conditions. Here, the gas evolution was reasonably rapid without added base but the rate did not increase when triethylamine was added. The products included no detectable amount of 2,3-diphenylcyclopropenone. Instead, the ether and aldehyde which result from the solvolysis of the corresponding cyclopropenyl chloride were obtained.

TABLE 2. ACID CHLORIDE 4-PICOLINE N OXIDE REACTION PRODUCTS IN ACETONITRILE[a]

| *Catalyst*[b] | *Acid chloride* | *Ratio*[c] | *$CO_2$*[g] | *Ketone*[g] | *Picolinium salt*[g] | *Other*[g] |
|---|---|---|---|---|---|---|
| Triethylamine | Diphenylacetyl | 1·05 | 0·52 | 0·33 | 0·065 | *d* |
| Triethylamine | Diphenylacetyl | 2·07 | 0·52 | 0·39 | 0·068 | *d* |
| Triethylamine | Diphenylacetyl | 4·19 | 0·69 | 0·66 | 0·030 | *d* |
| Triethylamine | Diphenylacetyl | 9·00 | 0·69 | 0·65 | — | |
| Pyridine | Diphenylacetyl | 0·97 | 0·56 | 0·21 | 0·065 | 0·26[e] |
| Pyridine | Diphenylacetyl | 1·88 | 0·63 | 0·50 | 0·093 | 0·11[e] |
| Pyridine | Diphenylacetyl | 3·87 | 0·60 | 0·62 | 0·062 | 0·06[e] |
| Pyridine | Diphenylacetyl | 10·68 | 0·47 | 0·61 | | |
| None | Diphenylacetyl | 3·0 | 0·78 | 0·57 | | |
| Triethylamine | 9-Fluorenyl | 10·0 | | 0·72 | | |
| None | 9-Fluorenyl | 8·0 | 0·64 | 0·46 | | |
| Triethylamine | 2,3-Diphenylclopropenyl | 2·29 | 0·51 | Nil | | |

[a] Room temp, acid chloride concentrations 0·2 m.

[b] 1 Equivalent.

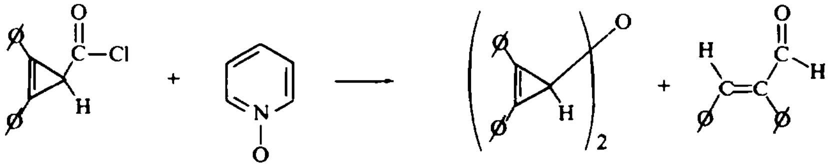
[c] N-oxide to acid chloride.

[d] 0·11–0·20 Equivalent of diphenylacetic acid recovered.

[e] N-Benhydrylpyridinium chloride.

[f] 2,3-Diphenylpropenal, *Bis*(2,3-diphenyl)cyclopropenyl ether.

[g] Moles/mole.



Finally, a brief study of the reaction of oxygen-18 enriched diphenylketene was carried out. These results, summarized in Table 3 indicated that the carbon dioxide is formed from one oxygen of the ketene and one oxygen from an N-oxide and that the ketone arises solely by oxygen transfer from the N-oxide to the α-carbon of the ketene.

TABLE 3. OXYGEN-18 DISTRIBUTION[a] IN REACTIONS WITH 4-PICOLINE N-OXIDE

| *Starting material* | | *$CO_2$* | *Benzophenone* |
|---|---|---|---|
| Diphenylacetyl Chloride | 0·788 | 1·07 | 0·208 |
| Diphenylketene | 0·788 | 1·06 | 0·209 |

[a] Numbers listed are atom % oxygen-18 per molecule.

## DISCUSSION

The complexity of the products formed in these reactions detracts generally from the conclusions which can be drawn. The carbon dioxide and polymer yields are particular problems. The gas evolution as measured by volumetric methods was found to be rather irreproducible unless the reaction was carried out under reflux. This could be an indication that some of the intermediates involved in the polymerization process carbonate reversibly, as with the primary amine-carbamic acid system.

The reaction of the cyclopropene carbonyl chloride seems to fit expectations for path A (Chart I) with collapse of the cyclopropenium-chloride ion pair. It appears that the known[12] oxidation route available to alkyl halides and N-oxides is not sufficiently rapid to give the ketone under the present conditions. The most interesting observation here is the absence of base catalysis in this case which is in accord with the low acidity expected for the α-proton of the cyclopropenyl structure. The $^{18}O$ results do not allow a distinction between mechanisms A–D but do suggest that the operative path is among these possibilities.

Several additional conclusions seem to be apparent from the data of Tables 1 and 2. First, an intermediate is present in all of these reactions which is capable of reacting with both free amine (product or added) and amine N-oxide. This accounts for the less than quantitative yields of ketones. For the results under aprotic conditions (I), the ylide (**8**), which polymerizes alone or could be protonated if a proton source were available, might also react with the unknown electrophile in a fashion similar to the N-oxide itself. This would account for the relatively large amount of polymeric material formed in the purified diphenylketene reactions.

For the reactions with proton sources available (II) it is clear that the formation of the N-alkylated salts is a bi-molecular process and not an intramolecular or cage process as might be supposed. This follows since pyridine added to picoline N-oxide reactions, successfully competes for the unknown intermediate with both the N-oxide and the product 4-picoline. The fact that the ketone yields appears to level off at less than 100% is suggestive of the behavior of the recently reported reaction of acetyl peroxide with acetate salts.[13] This observation could be interpreted in terms of an intermediate which can undergo some intramolecular reaction which does *not* lead to ketone, in competition with first order formation of a second species which reacts to form ketone or pyridinium salts by second order processes. The reactions of the acid chloride-N-oxide complex is subject to base catalysis. This is most likely connected to the mechanism of formation of the active unknown intermediate.

The critical question is the identity of this apparently electrophilic species. Again, we were led to suspect the α-lactone as the most reasonable molecule which fulfils these requirements. We carried out one test of this possibility by decomposing di-t-butylperoxy-diphenylmalonate[14] in acetonitrile with and without added N-oxide. The yield of benzophenone was the same in both cases in agreement with the findings of Rüchardt.[6] However, it is not *absolutely* clear that the same α-lactone is formed in both cases. There exists the possibility that the two reactions give isometric (π and σ) forms of the same species which react differently.

With this possibility in mind, we investigated the predictions of EHT[15] and CNDO/2[16] molecular orbital methods to the isomerization (π → σ) of both α-lactone and the more familiar intermediate, cyclopropanone. The results of these calculations are summarized in Fig. 1.

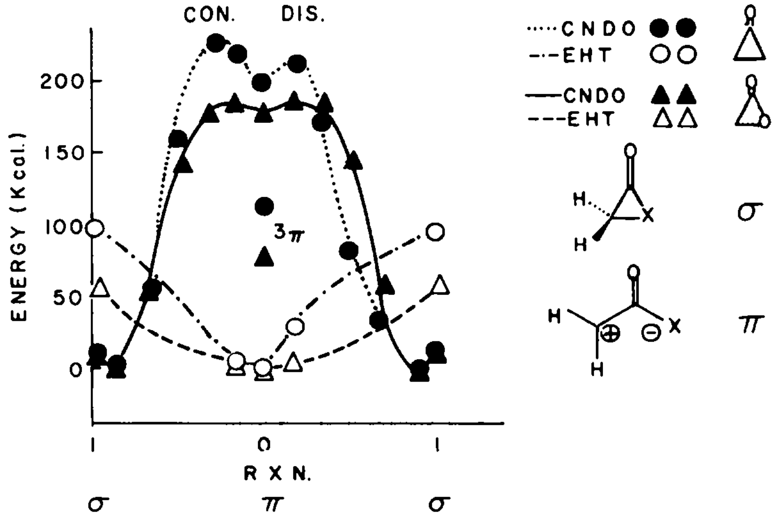


FIG. 1

The results of the CNDO2 calculations suggest that the $^1\sigma$ form of cyclopropanone is most stable. The angular geometry at the minimum appears to correspond to the recently published[17] microwave structure in that the $C_2$-$C_1$-$C_3$ angle is about 70°. The π form is predicted to be a ground state triplet.[*] The disrotatory mode of motion

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[*] The triplet state energies were calculated using a molecular overlap routine for tracking the state populated.

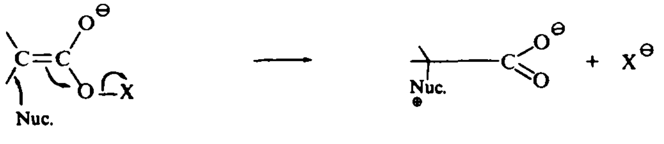
is predicted to be more facile as expected on the basis of symmetry. However, the magnitude of the energy barrier to the ${}^1\sigma \rightarrow {}^1\pi$ conversion calculated by this method, if taken literally, is too high to allow this process to be important in reactions starting from $\sigma$ cyclopropanones.[19] The results for the $\alpha$-lactone are similar except that the barrier to conversion of the ${}^1\pi$ form to the ${}^1\sigma$ form is very small. This suggests that while the ${}^1\pi$ form consists at a potential minimum, it would immediately decay to the ${}^1\sigma$ form. A ${}^3\pi$ form could be a distinct intermediate with a definite lifetime. The EHT results make directly opposite predictions in both cases, i.e. that the $\pi$ forms should be the most stable singlets.

The fact that the CNDO/2 method predicts the $\sigma$ form of cyclopropanone to be most stable, in agreement with experiment,[17] makes it appear to be a better method for estimating such angular barriers than EHT. The importance of electron-electron repulsion, which is neglected completely with the EHT method, seems to be clearly demonstrated by the contrast in the two potential energy profiles. However, the absolute magnitudes of the barriers predicted by the CNDO/2 method are probably not very reliable.[20] Therefore, the possibility that $\sigma$ cyclopropanone can isomerize to the $\pi$ form at accessible temperatures remains in spite of the prediction to the contrary by these CNDO/2 calculations. Similarly, the possibility that the $\pi$ and $\sigma$ forms a $\alpha$-lactone could be separate entities with finite lifetimes remains in spite of the low barrier predicted by the CNDO/2 method. The general *form* of the energy profile in which the $\pi$ form does exist at a potential minimum could be taken as evidence for this situation if the predicted magnitude of the rotational barrier is not taken too seriously.

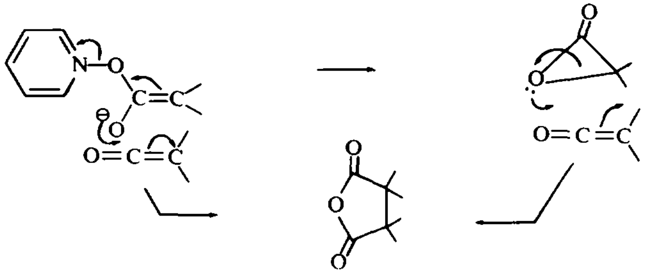
The polymerization of an $\alpha$-lactone species might also be catalyzed by radicals. Thus, the radical conditions for generation of the *same* form of the $\alpha$-lactone might lead to a lower concentration of the species and thus reduce the probability that it reacts with the N-oxide. The radicals present might be more efficient scavengers of such an intermediate than the N-oxide. The negative evidence against this possibility is thus not completely conclusive.

A carbene species could also fulfill the role of the unknown intermediate. No evidence of trapping of this species was obtained when ethyl vinyl ether was present during the reaction of the distilled ketene and pyridine N-oxide. However, this carbene might react more efficiently with the N-oxide[21] or amine than with the olefin. Thus the absence of any trapping product is also ambiguous for the present.

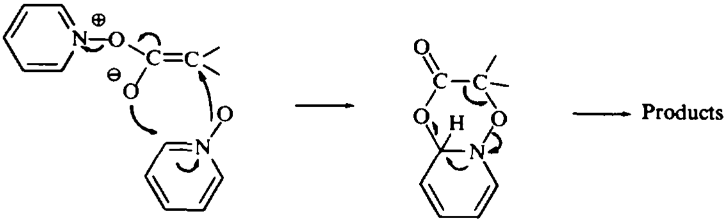
The enolate species (5) could fulfill the role of the unknown if one postulates that the attack of a nucleophile at a carbon bearing a partial negative charge is a rapid process when an elimination is possible. This seems contrary to intuition.

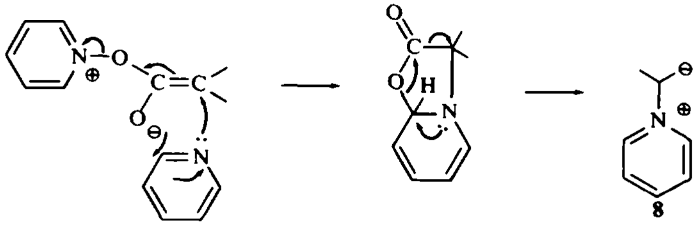


The form of the bis-biphenylene succinic anhydride can be rationalized as either the trapping of the α-lactone by the ketene or by a dipolar addition-elimination between the enolate and the ketene.



A similar dipolar addition-elimination process could actually be involved in the formation of the ketone and ylide (8) as well.

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This dipolar route furnishes a rationalization of how the enolate species (5) with partial negative charge at the α-carbon could apparently function as an electrophile with less intuitive objection.*

The reactions studied here appear to be different from the anhydride N-oxide reaction in that very little of the ylide (8) or products derived from it appear to be formed when anhydride is present in appreciable concentration. The role of the carboxylic acid in the anhydride reactions is a question which still remains to be answered. The differences in the products formed under the seemingly minor differences in conditions is probably connected to these answers and must await further work. It is hoped that a sharper distinction between these possibilities will be possible then. As of the present, the enol, enolate and α-lactone all could be involved depending on the proton donating ability and other properties of the substrate end medium.

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* Against the dipolar route is the preliminary result obtained in these laboratories of some ketone formation from diphenylketene and trimethylamine N-oxide. Further studies of this reaction are required before the results can be considered conclusive.

## EXPERIMENTAL

The IR spectra were measured with a Beckman IR7 or IR5. The NMR spectra were measured with a Varian A-60. The GLC was done on an Aerograph 600D. The mass spectra of the $^{18}O$ labeled $CO_2$ were determined using a modified CEC-21-614 residual gas analyzer. The mass spectrum of bis-biphenylene-succinic anhydride was obtained with a CEC-110B mass spectrometer.

*Materials.* The diphenylacetyl chloride was prepared from diphenylacetic acid (Aldrich) by treatment with excess thionyl chloride. The 4-picoline-N-oxide (Aldrich) was recrystalized from acetonitrile and dried at 90° (m.p. 184–185°). The pyridine-N-oxide was distilled directly into the reaction vessel. The acetonitrile (Matheson-Coleman and Bell) was distilled from phosphorous pentoxide (b.p. 81–82°) and stirred over activated Linde molecular sieves.

*Oxidation of distilled diphenylketene*[22, 23] (Table 1). In a typical run a soln of diphenylketene (36·5 mmol) in 50 ml acetonitrile was added dropwise to a refluxing soln of 4-picoline-N-oxide (160 mmol) in 60 ml acetonitrile under $N_2$. After 3 hr the yield of $CO_2$ (30·4 mmol) was determined by using a gas buret. Then the solvent was removed *in vacuo* and the residue dissolved in $CHCl_3$. After washing this soln successively with 10% HClaq and 10% NaOHaq the amount of benzophenone (11·2 mmoles) in the soln was determined by quantitative IR spectroscopy using the CO band at 1665 $cm^{-1}$. In some runs the amount of this product was determined by quantitative NMR using dioxan as an integration standard.

The $CHCl_3$ soln was evaporated *in vacuo* and the residue was chromatographed on Florisil. Elution with ligroin (30°/60°) yielded 2·6 g benzophenone (identified by IR). Elution with $CHCl_3$ gave 2·35 g material (m.p. 150–260°); NMR ($CDCl_3$) broad multiplet 7$\delta$ to 8$\delta$.

*Oxidation of* in situ *generated diphenylketene.* In a typical run a soln of diphenylacetyl chloride (2·52 mmol) and $Et_3N$ (2·52 mmol) in 10 ml acetonitrile was added to a soln of 4-picoline-N-oxide (5·82 mmol) in 20 ml acetonitrile under $N_2$ at room temp. The reaction mixture was purged with $N_2$ for 24 hr and the evolved $CO_2$ (2·05 mmol) was absorbed on Ascarite after passing through $H_2SO_4$ and a spray trap.

Then the solvent was evaporated *in vacuo* and the residue, dissolved in $CHCl_3$, was successively washed with 10% HClaq and 10% NaOHaq. The yield of benzophenone (0·90 mmol) was determined by GLPC (SE-30 at 120°) of the residue. The HCl wash was neutralized, evaporated *in vacuo*, and the residue extracted with $CHCl_3$. The $CHCl_3$ soln was evaporated *in vacuo* and a known amount dissolved in $CDCl_3$ containing dioxan. An NMR spectrum revealed the presence of N-benzhydryl-4-picolinium chloride (doublet ($J$ = 6$H_z$; 2H) at 9·25 $\delta$; singlet (1H) at 8·26 $\delta$; doublet ($J$ = 6$H_z$; 2H) at 6·05 $\delta$; multiplet (10H) at 7·33 $\delta$; singlet (3H) at 2·68 $\delta$) (0·48 mmol by integration of NMR spectrum).

The other runs were modified as shown in Table 1. The product analysis was the same except in the runs noted the $CO_2$ yield was measured with a gas buret. This method was found to give erratic results with room temp reactions using aceonitrile.

*Biphenylene ketone reaction.* (Table 1) In a typical run a soln of fluorene-9-carbonyl (91·5–93°; lit. 90–90·5°;[10] 3·86 mmols) in 25 ml acetonitrile was added to a soln of 4-picoline-N-oxide (27·5 mmol) in 50 ml acetonitrile under $N_2$ at room temp over a period of 45 min. For 3 hr the reaction mixture was purged with $N_2$ and the evolved $CO_2$ (2·34 mmol) was absorbed on Ascarite after washing with $H_2SO_4$. Then anhyd HCl was added until the blue color of the soln was dissipated. The soln was then evaporated *in vacuo*, and a dichloromethane soln of the residue was washed with water.

The yield of fluorenone (1·19 mmol) was determined by GLPC (SE-30 at 140°), and the yield of *bis*-biphenylene succinic anhydride (0·67 mmol) by the comparison of the IR absorbance at 1730 $cm^{-1}$ with a soln of authentic material. The anhydride was separated from 9-fluorenone by extracting the latter into ligroin (30°/60°) and recrystalizing the residue from dioxan (m.p. 269–270°; mixed m.p. 269–270°).

*Preparation of* bis-*biphenylene succinic anhydride.* A solution of bis-biphenylene succinyl chloride[24] (1·94 mmol), (m.p. 211–212°) water (1·95 mmol), and pyridine (2·53 mmol) in 10 ml acetonitrile was heated for 12 hr at 60°. Then the solvent was evaporated and the residue recrystalized from EtOAc (1·6 mmol) (m.p. 180°–240°). Then it was recrystalized from dioxane twice (m.p. 269–270°); mass spectrum, M = 400 (Calc. for $C_{28}H_{16}O_3$: M = 400). (Found: C, 82·10; H, 3·92. Calc. for $C_{28}H_{16}O_3$: C, 83·99; H, 4·01%).

*Triethylamine catalyzed oxidation of diphenyl acetyl chloride.* In a typical reaction a soln of diphenylacetyl chloride (21·90 mmol) in 20 ml acetonitrile was added to a soln of 4-picoline-N-oxide (22·90 mmol) in 60 ml acetonitrile under $N_2$ at room temp over a period of 5 min. Then a soln of $Et_3N$ (22·90 mmol) was added dropwise.

The reaction mixture was purged with $N_2$ for 24 hr and the evolved $CO_2$ (11·4 mmol) was absorbed on Ascarite. Then 8 ml of 10% HCl was added to the reaction mixture and the soln was evaporated *in vacuo*. The residue was dissolved in $CH_2Cl_2$ and extracted successively with water and 10% KOHaq. The $CH_2Cl_2$

soln was evaporated under reduced press. The residue was dissolved in $CHCl_3$ and its benzophenone (7·23 mmol) content determined by the IR method. The yield of N-benzhydryl-4-picolinium chloride (1·42 mmol) was determined by the NMR technique.

The runs with added pyridine were carried out in a similar fashion except for the NMR analysis of the N-benzhydrylpyridinium and picolinium salts. The total yield was determined by the relative areas of the $\alpha$ protons peak (ca. 9·25δ) compared to a known amount of dioxan. The relative amount of 4-picolinium and pyridinium components was determined by the ratio of the area of the Me singlet (7·33δ) of the picolinium salt to the total peak area of the $\alpha$-protons.

*Oxidation of fluorene-9-carbonyl chloride.* A soln of fluorene-9-carbonyl chloride[10] (4·26 mmol) in 15 ml acetonitrile was added to a soln of 4-picoline-N-oxide (31·9 mmol) in 60 ml acetonitrile at room temp under $N_2$ over a period of 4 min.

The reaction mixture was purged with $N_2$ for 3 hr and the evolved $CO_2$ (2·71 mmol) was absorbed on Ascarite. The solvent was removed *in vacuo* and the residue was dissolved in $CH_2Cl_2$ and extracted successively with 10% HClaq and 10% KOHaq. The $CH_2Cl_2$ soln was evaporated *in vacuo* and the residue dissolved in $CHCl_3$. Its 9-fluorenone (1·97 mmol) content was determined by the quantitative IR method. The bis-biphenyl succinic anhydride yield (0·50 mmol) was determined by its IR absorbance at 1795 $cm^{-1}$.

The colourless 10% HCl soln was made basic with KOH and an intensely blue compound was extracted into $CHCl_3$. Upon drying the $CHCl_3$ soln and treatment with HCl, the soln became colorless. The solvent was removed *in vacuo* and an NMR spectrum of the residue in $CDCl_3$ was identical to that of N(9-fluorenyl)-4-picolinium chloride.

*Oxidation of 2,3-diphenylcyclopropene-1-carbonyl chloride*[14]. The acid chloride (6·01mmol) in 20 ml acetonitrile was added to a soln of 4-picoline-N-oxide (13·2 mmol) in 40 ml acetonitrile at room temp. The reaction mixture was purged with $N_2$ for 24 hr and the $CO_2$ (3·08 mmol) was absorbed on Ascarite after passing through $H_2SO_4$ and a spray trap. Then the solvent was removed *in vacuo* and the residue chromatographed on florisil. After elution with a soln of ligroin (30°/60°) and EtOAc and subliming the eluate, *trans*-2,3-diphenylpropenal (1·44 mmol; m.p. 94–95°; lit.[25] 94–95°) was isolated. Bis-2,3-diphenylcyclopropenyl ether (m.p. 170–171°; lit.[26] 170–172°) was also isolated. This ether is reported[6] to give *trans*-2,3-diphenylpropenal when chromatographed on alumina.

$^{18}O$ *Studies.* The $^{18}O$ labeled diphenylacetyl chloride was prepared by hydrolysis of the acid chloride and resubjecting the product acid to thionyl chloride. An aliquot of this material was used directly in condition III. The $CO_2$ was collected in a liquid $N_2$ trap. The benzophenone was isolated by recrystallization of the neutral residue.

A second aliquot of the $^{18}O$ labeled acid chloride was used to generate diphenylketene under condition II ($Et_3N$). The $CO_2$ and ketone were isolated as above. The $^{18}O$ contents of the acid chloride and benzophenone were determined as $CO_2$.[27]

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