we hestitate to assign this σ^+ value on the basis of these data since pK_4 for **1** is very close to the thermodynamic constant and the other p$K'_{\mathrm{BH^+}}$ values may not be.

Experimental Section

The sulfonated azobenzenes **1**, **2**, **4**, and **16** were Eastman grade or Eastman Certified grade products that were recrystallized to constant absorption curves. Compound **3** was prepared from **2**, and **5** was obtained by sulfonation of *p*-chloroazobenzene. The phenylazonaphthols were prepared in the usual way.

The methyl ethers of **9** and **10** (**13** and **14**) were prepared by reaction of the dyes with methyl iodide in DMF containing a small amount of aqueous sodium carbonate. Methyl orange was quaternized by warming the dye with a large excess of methyl iodide in DMF. The very insoluble inner salt precipitated from the reaction medium and was purified by repeated digestions with 50% ethanol on a steam bath. The diphenylhydrazone **15** was prepared by condensation of 1,2-naphthoquinone with 1,1-diphenylhydrazine in aqueous acetic acid, mp 173–175° (lit.[41] mp 171–172°). All compounds except **14** gave elemental analyses within 0.3% of the theoretical for at least two elements.

Baker and Adamson reagent grade sulfuric acid gave the most reproducible results. At the low concentrations of substrates used here (2.5×10^{-6} *M*), trace impurities present in other sources of acid caused partial reduction of the substrates. The acid solutions were prepared by diluting predetermined volumes of concentrated acid, delivered from a buret. Replicate determinations of indicator ratios in solutions prepared by this method gave identical results. The acidity function values, H_i, corresponding to a given acid concentration were obtained from large plots of H_i against weight per cent sulfuric acid. The values of H_0 given by Paul and Long[24] were used up to 60% acid. At higher acidities, the H_0 values determined by Jorgenson and Hartter[1] were used.

The absorption curves were measured on a Cary Model 14 spectrophotometer over a sufficiently wide wavelength range to include the bands characteristic of both the azo and the azonium species. To avoid deviations from Beer's law the concentration of azo compound was 2.5×10^{-6} *M*; 10-cm cuvettes were used for the measurements.

Acknowledgments. The author is indebted to Dr. P. T. S. Lau and to Messrs. A. Loria and G. Brown, for supplying many of the compounds used in this study, to Dr. G. J. Wernimont, for invaluable aid in the numerical analysis, and to Mr. R. W. Andrus, for technical assistance.

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Phenyldiimide. III. Ferric Ion Catalyzed Formation of Free Radicals in Heterolysis of Azo Compounds[1,2]

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Received December 29, 1965

Abstract: Ferric ion catalyzes effectively the methanolysis of N-phenyl-N′-benzoyldiimide ($C_6H_5N{=}NCOC_6H_5$, I) leading to higher yields of methyl benzoate and phenyldiimide ($C_6H_5N{=}NH$, II) than the acid- or base-catalyzed reactions. The ferric ion oxidizes II efficiently, minimizes its reaction with I, and leads to high yields of phenyl radical from I at room temperature. In methanol the phenyl radical is converted to benzene, in the presence of benzene to biphenyl, in the presence of nitrobenzene to nitrobiphenyls, and in the presence of carbon tetrachloride to chlorobenzene in high yield. Ferric ion catalyzed methanolyses of compound I, of N,N′-dibenzoyldiimide ($C_6H_5CON{=}NCOC_6H_5$, III), and of diethyl azodicarboxylate ($C_2H_5O_2CN{=}NCO_2C_2H_5$, IV) lead to free radicals which add to acrylonitrile and initiate its polymerization more effectively than the acid-catalyzed methanolyses of these azo compounds.

Early attempts to prepare and isolate aryldiimides (Ar—N=N—H) led to nitrogen and the hydrocarbons ArH, and to the conclusion that the diimides were unstable and decomposed to these products.[3] Phenyldiimide ($C_6H_5N{=}NH$) has been suggested as an intermediate in the oxidation of phenylhydrazine; when the oxidation was carried out in water, only benzene and nitrogen were isolated.[4] When ether[5a] or phenylhydrazine[5b] itself was solvent other products were isolated, including biphenyl. Subsequently, oxidation of phenylhydrazine[6] and of pentafluorophenylhydrazine[7] in aromatic solvents led to appropriate biaryls, indicating that phenyl and pentafluorophenyl radicals had been formed by decomposition of or by oxidation of the diimides.

We have recently reported[2] that the thermally stable compounds N-phenyl-N′-carbethoxydiimide ($C_6H_5N{=}NCO_2C_2H_5$) and N-phenyl-N′-benzoyldiimide ($C_6H_5N{=}NCOC_6H_5$, I) undergo rapid acid- or base-catalyzed alcoholysis and lead to free phenyl radicals, presumably *via* phenyldiimide II. Detailed investigations of the parent compound, diimide HN=NH, have been reported in recent years.[8–10] Some spectral observa-

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[1] We are pleased to acknowledge generous support of this work by the National Science Foundation, GP 1833, and predoctoral fellowships under title IV of the National Defense Education Act, and of the National Institutes of Health, GM 24864.

(2) For previous reports, see S. G. Cohen and J. Nicholson, (a) *J. Am. Chem. Soc.*, **86**, 3892 (1964); (b) *J. Org. Chem.*, **30**, 1162 (1965).

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tions consistent with formation of a relatively long-lived species that may be phenyldiimide have been reported recently.[11]

Unequivocal evidence for the formation of phenyl radicals from I is seen in the formation of substantial yields of biphenyl, chlorobenzene, the nitrobiphenyls, the phenylnaphthalenes, and polyacrylonitrile when the methanolysis of I is carried out in the presence of benzene, carbon tetrachloride, nitrobenzene, naphthalene, and acrylonitrile, respectively.[2] In the absence of such additives methanolysis of low concentrations (<0.01 *M*) of I leads to high yields of nitrogen (*ca.* 90%) and methyl benzoate, and a moderate yield of benzene. At higher concentrations (~ 0.1 *M*) of I these yields drop markedly as the products of addition of phenyl and hydrogen to I, the diphenylbenzoylhydrazines, are formed in competition with the heterolysis of I. Similarly if fumaric acid is present during the methanolysis of I a high yield of phenylsuccinic is obtained.[2]

It seemed that this formation of phenyl radicals, species which must participate in some of these reactions and which may be involved in all of them, may be a process largely dependent upon oxidation–reduction reactions, and that addition of a known oxidizing agent would affect and give information about the course of these reactions. We now report on the effect of ferric ion on the formation of free radicals in the heterolysis of azo compounds.

Results

Addition of a solution of $Fe(NO_3)_3 \cdot 9H_2O$ in methanol to a methanol solution of N-phenyl-N′-benzoyldiimide I at room temperature led to rapid decomposition of I, with discharge of its color and evolution of nitrogen, reduction of ferric to ferrous ion, and formation of methyl benzoate and benzene in good yield (Table I). Reduction of ferric to ferrous ion was indicated by addition of potassium cyanide and examination for the color of prussian blue.[12] In experiments Fi and Fii in which the initial molar quantities of ferric ion were 52 and 76% as great as that of I, the color test was negative, all the ferric ion having been reduced. Addition of ferric ion to the test solutions then led to the color. In these experiments the yields of methyl benzoate were 65 and 81%, respectively, and the yields of phenyldiimide were probably similar as indicated in eq 1, below. The yields of benzene were somewhat lower, 40 and 70%, respectively. When the initial quantity of ferric ion was 92% as great as that of I, Fiii, the color developed when cyanide was added, indicating that both ferric and ferrous ion were present and that between 76 and 92% molar equiv of ferric ion is reduced in the ferric ion catalyzed methanolysis of I. When excess ferric ion was present the yield of methyl benzoate was quite high, 87%, and benzene appeared to be formed in about 65% yield. In other ferric ion catalyzed methanolyses of I, solutions were examined for phenol, none being found, and for anisole, about 5% yield being found. Some results are summarized in Table I and compared with that of a hydrochloric acid catalyzed methanolysis of I.

Table I. Methanolysis of $C_6H_5N{=}NCOC_6H_5$ (I). Effect of $Fe(NO_3)_3$

Expt no.	—Compound I— Mmole	*M*	$Fe(NO_3)_3$, Mmole	$C_6H_5CO_2CH_3$ Mmole	%	C_6H_6, %	Color test
Fi	0.32	0.11	0.17	0.21	65	40	Neg
Fii	0.34	0.074	0.26	0.28	81	70	Neg
Fiii	0.18	0.061	0.17	0.16	87	65	Pos
Fiv	0.28	0.12	0.23	0.22	79	*a*	. . .
Fv	0.98	0.20	0.50	0.73	74	*b*	. . .
Hi	0.38	0.076	*c*	0.23	62	35	. . .

[a] 6% yield of anisole. [b] 4% yield of anisole. [c] 0.6 mmole of HCl, no Fe^{3+}.

Silver ion also was reduced during methanolysis of I. Methanolysis was considerably slower in the presence of silver nitrate than in the presence of hydrochloric acid or of ferric nitrate. Metallic silver was deposited, and in the presence of 25% excess silver ion a 79% yield of silver was obtained, based on the initial quantity of compound I, corresponding well to the extent of reduction of ferric to ferrous ion.

That high yields of free phenyl radical are formed in the ferric ion catalyzed methanolysis of I is seen in experiments in which the presence of additives diverts the radical in large part to products other than benzene. Some results are summarized in Table II, including results of comparable methanolyses catalyzed by HCl.

In each case, in the presence of benzene, nitrobenzene, and carbon tetrachloride, 70% Fe^{3+} based on compound I leads to 78 to 92% yields of methyl benzoate, and presumably to comparable yields of phenyldiimide, as compared to 40 to 60% yields when the methanolyses are catalyzed by hydrochloric acid, or by 10 mole % Fe^{3+}. The yields of products derived from phenyl radical also were substantially higher in the presence of 70 mole % Fe^{3+} as compared with results in the presence of 10% Fe^{3+} and in the presence of hydrochloric acid. Yields of 47% biphenyl, 44% nitrobiphenyl, and, in particular, 71% chlorobenzene indicate quite significant yields of phenyl radical. The yield of benzene was uniformly reduced to about 10%.

Effects of ferric and other salts on the polymerization of acrylonitrile initiated by heterolysis of three azo compounds have been examined briefly. Aliquots (5 ml) of acrylonitrile solutions of the azo compounds were treated with 1 ml of methanol solutions of the metal salts, or with 0.5 ml of concentrated hydrochloric acid, and the polymer was precipitated, weighed, and examined spectrophotometrically. The results are summarized in Table III. Blank experiments in which the acrylonitrile was treated, without an azo compound, with solutions of the salts or with hydrochloric acid led to no polymer.

With compound I ($C_6H_5N{=}NCOC_6H_5$) ferric nitrate led to 50% more polymer than did hydrochloric acid, 25 and 16% yields, respectively. Magnesium nitrate was ineffective; it did not catalyze the methanolysis of I and led to neither radicals nor polymer. Ferric chloride was less effective than either ferric nitrate or hydrochloric acid. Zinc chloride and aluminum chloride catalyzed decomposition of I and led to polymer to about the same extent as hydrochloric acid. Dibenzoyl-

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Table II. Methanolysis of $C_6H_5N{=}NCOC_6H_5$ (I) in the Presence of Additives. Effect of $Fe(NO_3)_3$

Expt no.	Additive Compd	Additive M	Compd I, M	Fe^{3+}, M	% yield C_6H_5-CO_2CH_3	% yield Ph product	% yield C_6H_6
FBi	C_6H_6	7	0.32	0.032	55	33[a]	...
FBii	C_6H_6	7	0.17	0.12	92	47[a]	...
FNi	$C_6H_5NO_2$	6	0.32	0.032	55	23[b]	11
FNii	$C_6H_5NO_2$	6	0.16	0.12	86	44[c]	10
FCi	CCl_4	6	0.33	0.034	52	45[d]	8
FCii	CCl_4	6	0.17	0.12	78	71[d]	10
B-3	C_6H_6	11	0.17	...[e]	41	38[f]	...
N-1	$C_6H_5NO_2$	7	0.18	...[e]	57	32[g]	10
C-2	CCl_4	7	0.17	...[e]	58	40[h]	9[i]

[a] Biphenyl. Traces of azobenzene and anisole were found. [b] Combined yield of 2-, 3-, and 4-nitrobiphenyls, in ratio 6:1:8. Traces of biphenyl and anisole were found. [c] Combined yield of 2-, 3-, and 4-nitrobiphenyls, in ratio of 5:1:7. Azobenzene was found, 7%. [d] Chlorobenzene. Hexachloroethane and chloroform were found. [e] No Fe^{3+}; reaction catalyzed by HCl. See ref 2b. [f] Biphenyl. [g] Combined yield of 2-, 3-, and 4-nitrobiphenyl. See ref 2b. [h] Chlorobenzene; other products described in ref 2b. [i] Expt c-1. See ref 2b.

Table III. Polymerization of Acrylonitrile. Effects of Azo Compounds and Salts

Azo compd Formula	Azo compd M	Catalyst Formula	Catalyst M	Polymer, %
PhN=NCOPh	0.035	$Fe(NO_3)_3$	0.017[a]	25
PhN=NCOPh	0.035	$Mg(NO_3)_2$	0.025[a]	0
PhN=NCOPh	0.035	$FeCl_3$	0.017[a]	10
PhN=NCOPh	0.038	HCl	1.0[b]	16
PhN=NCOPh	0.035	$ZnCl_2$	0.017[a]	13
PhN=NCOPh	0.035	$AlCl_3$	0.017[a]	19
PhCON=NCOPh	0.031	$Fe(NO_3)_3$	0.017[a]	25
PhCON=NCOPh	0.034	HCl	1.0[b]	1
$EtO_2CN{=}NCO_2Et$	0.040	$Fe(NO_3)_3$	0.017[a]	30
$EtO_2CN{=}NCO_2Et$	0.044	HCl	1.0[b]	15

[a] 12.5 *M* acrylonitrile, 4.2 *M* methanol. [b] 11.6 *M* acrylonitrile, 3 *M* water, 3.9 *M* methanol.

diimide ($C_6H_5CON{=}NCOC_6H_5$, III) also led to 25% polymer in the presence of ferric nitrate, but to only 1% in the presence of hydrochloric acid, showing remarkable dependence upon the presence of the oxidant. Diethyl azodicarboxylate (IV) led to results similar to those with compound I, 30% polymer in the presence of ferric nitrate, 15% in the presence of HCl.

The samples of polyacrylonitrile were examined spectrophotometrically and compared with a sample prepared with a hydrogen peroxide–ferrous ion initiator. Polymers prepared from an azo compound in hydrochloric acid and ferric ion catalyzed reactions were identical with each other and different from that prepared without an azo compound. Polymer prepared with N-phenyl-N′-benzoyldiimide (I) showed very weak carbonyl absorption at 6.0 μ, monosubstituted phenyl bands at 13.2 and 14.2 μ, and absorption at 235 and 330–360 mμ, perhaps due to phenyl and phenylazo groups. These infrared and ultraviolet bands were absent in polymer prepared with hydrogen peroxide as initiator. Polymer prepared with dibenzoyldiimide as initiator showed a strong carbonyl band at 5.95 μ and other bands in the infrared similar to polymer prepared from compound I. Polymer prepared with diethyl azodicarboxylate showed a strong carbonyl band at 5.78 μ. All polymers prepared with the azo compounds showed very weak hydroxyl absorption at 2.8–3.0 μ.

Discussion

The acid- or base-catalyzed methanolysis of I presumably leads initially to methyl benzoate and phenyldiimide II. At moderate initial concentrations of I (~0.1 *M*), this reaction does not proceed to completion since, in competitive processes, a substantial fraction of I is converted[2] to N,N′-diphenyl-N-benzoylhydrazine and to N,N-diphenyl-N′-benzoylhydrazine. This occurs by reaction of I with a molecule of II in a one-step or two-step reaction, or possibly by a sequence of free-radical reactions, or by both routes. With increasing concentration of I the yield of methyl benzoate may fall[2] from 85 to about 40%, and that of benzene from about 60 to as low as 12%.

$$\underset{\text{I}}{C_6H_5CON{=}NC_6H_5} + CH_3OH \xrightarrow{H^+\ (OH^-)} C_6H_5CO_2CH_3 + \underset{\text{II}}{C_6H_5N{=}NH}\ (C_6H_5N{=}N^-) \quad (1)$$

Ferric nitrate catalyzed the methanolysis of 0.07 *M* I, and resulted in about 80% reduction of ferric to ferrous based on the initial amount of I. When the yield of methyl benzoate (Table I), and thus of phenyldiimide, exceeded the amount of ferric ion initially present, reduction to ferrous was complete. Reduction of silver ion to silver metal in 79% yield was similarly observed when the methanolysis of I was carried out in the presence of excess silver nitrate. The ferric ion raised the yield of methyl benzoate to 81–87% and of benzene to 65–70%, yields at least as high as those observed in the absence of added oxidant only at initial concentrations of I an order of magnitude lower. It appears that phenyldiimide, formed in reaction I, is in large part oxidized by ferric ion to the phenyldiimide radical which decomposes to phenyl radical and nitrogen. The phenyl radical is then largely converted to benzene. A small part of the phenyldiimide and phenyl radical may still add to I, since the yield of methyl benzoate is not quantitative, and the yield of benzene is less than that of methyl benzoate. The phenyl radical is not substantially oxidized by ferric ion under these experimental conditions, since only low yields of anisole are obtained.

$$C_6H_5N{=}NH + Fe^{3+} \longrightarrow C_6H_5N{=}N\cdot + Fe^{2+} + H^+ \quad (2)$$

$$C_6H_5N{=}N\cdot \longrightarrow C_6H_5\cdot + N_2 \quad (3)$$

This efficient methanolysis might indicate that the addition of phenyl and hydrogen to I in the absence of oxidant proceeds by reaction of I with phenyldiimide and not of I with phenyl radical. On the other hand this might result simply if the ferric ion catalyzed methanolysis is very rapid, leaving little or no compound

I to react with II or with phenyl radical. The correspondence in yield of methyl benzoate, and so phenyldiimide, with that of ferrous ion or silver metal indicates that oxidation of phenyldiimide (eq 2) does not initiate a chain decomposition of phenyldiimide to benzene and nitrogen, in which reaction 3 would be followed by abstraction of hydrogen from phenyldiimide by phenyl radical.

The effects of ferric nitrate in increasing the yield of phenyl radical from compound I, and the products derived from this radical, are seen clearly in the high yields of methyl benzoate and in the yields of biphenyl, the nitrobiphenyls, and chlorobenzene in reactions carried out in 2:1 benzene–methanol, 2:1 nitrobenzene–methanol, and 2:1 carbon tetrachloride–methanol, respectively (Table II). The yields of biphenyl (47%) and of the nitrobiphenyls (44%) obtained in the presence of 70 mole % ferric nitrate, based on the amount of compound I undergoing methanolysis, are higher than the yields in the absence of ferric nitrate. They do not reflect the total yields of phenyl radicals, which must be substantially greater, since the initial products of arylation, phenylhexadienyl type radicals, may not be converted quantitatively to the isolated products. The product from phenyl radical in the presence of carbon tetrachloride, chlorobenzene, is formed in a single step and was isolated in 71% yield. This is very high, when compared with the yield of methyl benzoate in this experiment, 78%. The latter represents the maximum possible yield of phenyldiimide and of phenyl radical in this experiment. The small remainder of the phenyldiimide appears as benzene in this experiment, thus accounting for all the phenyldiimide—of which 90% was converted to phenyl radical in the presence of the ferric nitrate. When only 10 mole % ferric nitrate was present the results were similar to those in the acid-catalyzed reactions. The ferric salt is used on an equivalent basis in oxidizing phenyldiimide (eq 2), the negligible effect of the small amount providing further evidence that oxidant does not start a chain decomposition of the diimide.

The high yield of phenyl radical in the presence of ferric nitrate, clearly established in the presence of carbon tetrachloride, must also occur in methanol in the presence of ferric nitrate and absence of additives, when benzene is the major product (Table I). In that case much of the benzene results from abstraction of hydrogen from methanol by phenyl radical. However in the experiments in the presence of the oxidant for phenyldiimide and the scavengers for phenyl radical, and in the presence of 1.56 M fumaric acid which may react effectively with phenyldiimide,[2b] the yield of benzene fell and then remained constant at about 10%. This may reflect an independent, perhaps synchronous pathway for its formation from a form of phenyldiimide with which scavengers may not compete. Experiments with deuterium-labeled alcohols, now in progress, may give information about the courses of formation of benzene.

Results of polymerization of acylonitrile by methanolysis of I in the presence of ferric ion and other salts (Table III) are consistent with the proposed reactions. Ferric nitrate catalyzed methanolysis of I, acting as a Lewis acid, and increased the yield of phenyl radical, acting as an oxidant, leading then to more polymer than did hydrochloric acid. The acids zinc chloride and aluminum chloride which are not oxidizing agents led to no increase in polymer. The lower effectiveness of ferric chloride may be related to the capacity of radicals to abstract chlorine from this salt.[13]

Dibenzoyldiimide ($C_6H_5CON{=}NCOC_6H_5$, III) has been reported[14] to undergo homolytic decomposition and to initiate free-radical polymerization of acrylonitrile. The decomposition of III is accelerated by hydroxylic solvents and by acid catalysts, and this was attributed to acceleration of the radical reaction rather than to a shift to a rapid heterolysis,[14] a conclusion with which we do not fully agree. We find that the acid-catalyzed methanolysis of III leads to very little polymer ($\sim$1%). The ferric nitrate catalyzed methanolysis of III leads to polymerization as effectively as does that of compound I. The acid-catalyzed methanolysis may lead rapidly to benzoyldiimide ($C_6H_5CON{=}NH$, V) and then rapidly to diimide ($HN{=}NH$) which does not readily lead to hydrogen atoms. A slower alcoholysis in the absence of mineral acid[14] may have led to simultaneous presence of III and V in solution for a long enough period for oxidation of V by III to lead to radicals, and polymerization, but the yield of polymer was not reported.[14] The ferric nitrate catalyzed methanolysis of III apparently leads to V, then to oxidation of V by ferric ion, and to formation of benzoyldiimide radical and benzoyl radical which initiate polymerization

Diethyl azodicarboxylate (IV), which undergoes methanolysis less rapidly than III, and may be more like I in this respect, also leads to polymerization of acrylonitrile in the presence of both mineral acid and ferric ion at least to the same extent as I. This is noteworthy since hydrolysis of such compounds has hitherto led to diimide, and free radicals have not been reported.[8,9] Methanolysis of IV may lead to an intermediate diimide ($C_2H_5O_2CN{=}NH$) and thence apparently to the radicals $C_2H_5O_2CN{=}N\cdot$ and $C_2H_5O_2C\cdot$, formation of which is increased by presence of the added oxidant, ferric ion.

The samples of polyacrylonitrile prepared by methanolysis of the azo compounds I, III, and IV show absorption bands consistent with incorporation of the postulated initiator fragments—that from I shows evidence for phenyl and phenylazo groups, and little carbonyl absorption; that from III shows evidence for carbonyl and phenyl consistent with the presence of benzoyl groups; and that from IV shows carbonyl absorption consistent with ester end groups.

Summary. Phenyldiimide II may be formed in a variety of ways, by oxidation of phenylhydrazine[4,7] and by displacement and hydrolysis reactions of N-phenyl-N′-benzoyldiimide (I), N-phenyl-N′-carbethoxydiimide,[2] N-phenyl-N′-carboxydiimide,[2,11] and phenylazotriphenylmethane,[15] and it may be an efficient source of phenyl radicals. When it is formed by oxidation of phenylhydrazine, it is likely that the phenyl radicals arise by further oxidation of II to phenyldiimide radical ($C_6H_5N{=}N\cdot$) which loses nitrogen, rather than by thermal decomposition of II to phenyl, nitrogen, and hydrogen. When phenyl-

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[15] J. Nicholson and S. G. Cohen, unpublished results.

diimide is formed in the presence of manganese dioxide, it may be oxidized to phenyldiazonium ion and lead to phenyl cation.[16] When II is formed in base it may lead to phenyl anion.[17] When monosubstituted diimides are formed by heterolysis or displacement, presence of a mild oxidizing agent, such as ferric ion, leads to effective oxidation which may be followed by loss of nitrogen and formation of the appropriate free radical in high yield. In the absence of an added oxidant the initial azo compound, such as compounds I, III, and IV, or perhaps the diimide itself, may serve as the oxidant, leading to the free radical, but with less efficient use of the materials. Whether spontaneous decomposition of the diimide to the radical, nitrogen, and hydrogen atom occurs to an important extent under ordinary conditions is not clear. Phenyldiimide may be relatively stable and add efficiently the elements of benzene, phenyl, and hydrogen, to unsaturation—to N=N of the very source of the phenyldiimide, phenylbenzoyldiimide (I), and to the C=C of added fumaric acid.[2]

Experimental Section

N-Phenyl-N′-benzoyldiimide and N,N′-dibenzoyldiimide were prepared as described previously.[2] **Diethyl azodicarboxylate** had been prepared by Dr. R. Zand.[18]

Analyses by vapor phase chromatography were carried out as described previously.[2]

Ferric Ion Catalyzed Methanolysis of I. A stock solution of 0.056 *M* $Fe(NO_3)_3 \cdot 9H_2O$ in methanol was prepared and swept with argon. (i) A solution of 0.068 g (0.32 mmole, 0.108 *M*) of I in 3 ml of the Fe^{3+} stock solution (0.168 mmole of Fe^{3+}) was allowed to stand under argon for 2 hr, leading to a tan solution. A sample was treated with potassium cyanide, no color or precipitate forming. A few drops of the Fe^{3+} solution was added, leading to a purple color. Analysis by vapor phase chromatography indicated 0.029 g (0.21 mmole, 65% yield) of methyl benzoate and 0.010 g (0.13 mmole, 40% yield) of benzene.

(ii) A similar reaction of 0.0717 g (0.34 mmole 0.074 *M*) of I in 4.6 ml of the Fe^{3+} solution (0.26 mmole of Fe^{3+}) led to no color on treatment with potassium cyanide, color developing with addition of Fe^{3+} solution. Vapor phase chromatography indicated 0.0375 g (0.28 mmole, 81% yield) of methyl benzoate and 0.0186 g (0.24 mmole, 70% yield) of benzene.

(iii) A similar reaction of 0.0388 g (0.184 mmole, 0.061 *M*) of I in 3 ml of the Fe^{3+} stock solution (0.168 mmole of Fe^{3+}) led to the purple color on treatment with potassium cyanide. Vapor phase chromatography indicated 0.022 g (0.16 mmole, 87% yield) of methyl benzoate and 0.0093 g (0.12 mmole 65% yield) of benzene.

(iv) A similar reaction of 0.059 g (0.28 mmole, 0.12 *M*) of I in 2.3 ml of 0.10 *M* Fe^{3+} (0.23 mmole of Fe^{3+}) in methanol led to 0.030 g (0.22 mmole, 79% yield) of methyl benzoate, 0.0017 g (0.016 mmole, 6% yield) of anisole, and no phenol.

(v) A similar reaction of 0.205 g (0.98 mmole, 0.20 *M*) of I in 5.0 ml of 0.10 *M* Fe^{3+} (0.50 mmole of Fe^{3+}) led to 0.099 g (0.73 mmole, 74% yield) of methyl benzoate, 0.004 g (0.04 mmole, 4% yield) of anisole, and no phenol.

Methanolysis of I in the Presence of Benzene. (i) A solution of 0.330 g (1.58 mmoles) of I in 3 ml of benzene was allowed to react with 1.6 ml of 0.1 *M* Fe^{3+} in methanol (0.16 mmole of Fe^{3+}) for 2 hr, leading to gas evolution and brown coloration. Vapor phase chromatography indicated 0.118 g (0.87 mmole, 55% yield) of the methyl benzoate, 0.079 g (0.51 mmole, 33% yield) of biphenyl, and a trace of anisole.

(ii) A similar reaction of 0.057 g (0.27 mmole) of I in 1 ml of benzene with 0.5 ml of 0.37 *M* Fe^{3+} in methanol (0.19 mmole of Fe^{3+}) led to 0.034 g (0.25 mmole, 92% yield) of methyl benzoate, 0.020 g (0.13 mmole, 47% yield) of biphenyl, and traces of azobenzene and anisole.

Methanolysis of I in the Presence of Nitrobenzene. (i) A solution of 0.318 g (1.52 mmoles) of I in 3 ml of nitrobenzene was allowed to react with 1.5 ml of 0.1 *M* Fe^{3+} in methanol for 2 hr. A gas was evolved and analysis of the resulting purple solution by vapor phase chromatography led to 0.0295 g (0.147 mmole, 9.8% yield) of 2-nitrobiphenyl, 0.0045 g (0.0236 mmole, 1.5% yield) of 3-nitrobiphenyl, 0.0352 g (0.177 mmole, 11.6% yield) of 4-nitrobiphenyl, 0.0136 g (0.174 mmole, 11.4% yield) of benzene, 0.002 g (0.013 mmole, 1% yield) of biphenyl, and a trace of anisole. By elution chromatography, 0.114 g (0.84 mmole, 55% yield) of methyl benzoate was obtained.

(ii) A solution of 0.053 g (0.25 mmole) of I in 1 ml of nitrobenzene was treated with 0.5 ml of 0.37 *M* Fe^{3+} in methanol. Vapor phase chromatography, after 2 hr, indicated the presence of 0.0080 g (0.040 mmole, 16% yield) of 2-nitrobiphenyl, 0.0018 g (0.0091 mmole, 3.5% yield) of 3-nitrobiphenyl, 0.012 g (0.060 mmole, 24% yield) of 4-nitrobiphenyl, 0.0020 g (0.026 mmole, 10% yield) of benzene, and 0.0016 g (0.0088 mmole, 7% yield) of azobenzene. By elution chromatography, 0.0293 g (0.215 mmole, 86% yield) of methyl benzoate was obtained.

Methanolysis of I in the Presence of Carbon Tetrachloride. (i) A solution of 0.354 g (1.68 mmoles) of I in 3 ml of carbon tetrachloride was allowed to react for 2 hr with 1.7 ml of 0.1 *M* Fe^{3+} in methanol. Vapor phase chromatography indicated the presence of 0.119 g (0.87 mmole, 52% yield) of methyl benzoate, 0.085 g (0.75 mmole, 45% yield) of chlorobenzene, 0.011 g (0.14 mmole, 8.3% yield) of benzene, 0.010 g (0.043 mmole, 5% yield) of hexachloroethane, and a trace of biphenyl.

(ii) A solution of 0.055 g (0.262 mmole) of I in 1 ml of carbon tetrachloride was treated for 2 hr with 0.5 ml of 0.37 *M* Fe^{3+} in methanol. Vapor phase chromatography indicated the presence of 0.028 g (0.21 mmole, 78% yield) of methyl benzoate, 0.021 g (0.19 mmole, 71% yield) of chlorobenzene, and 0.0020 g (0.026 mmole, 10% yield) of benzene. Hexachloroethane and chloroform were also detected.

Methanolysis of I in the Presence of Silver Nitrate. A solution of 0.322 g (1.54 mmoles) of I in 15 ml of 0.13 *M* silver nitrate in 1:1 methanol–water was allowed to react for 2 days in the dark, a silver deposit forming. The silver was collected, 0.129 g (1.21 mmoles, 79% yield). The color of I persisted during much of this time.

Polymerization of Acrylonitrile. Stock solutions were prepared in freshly distilled acrylonitrile (Eastman Organic Chemicals) and stored under argon. Solution A contained 0.89 g (4.2 mmoles, 0.042 *M*) of I in 100 ml of acrylonitrile. Solution B contained 0.23 g (0.97 mmole, 0.039 *M*) of N,N′-dibenzoyldiimide in 25 ml of acrylonitrile. Solution C contained 0.21 g (1.14 mmoles, 0.046 *M*) of diethyl azodicarboxylate in 25 ml of acrylonitrile.

(i) A 5-ml aliquot of solution A and a 5-ml portion of acrylonitrile were treated separately with 1 ml of 0.106 *M* $Fe(NO_3)_3 \cdot 9H_2O$ in methanol under argon. The solution containing I became warm; polyacrylonitrile formed and was precipitated, 1.0 g, 25% yield. The blank remained unchanged after 1.5 hr, and dilution with methanol precipitated no polymer. The experiment was repeated, leading to identical results.

(ii) A 5-ml aliquot of solution A was treated with 1 ml of 0.15 *M* $Mg(NO_3)_2$ in methanol for 4 hr, leading to no polymer.

(iii) A 5-ml aliquot of solution A was treated with 1 ml of 0.10 *M* $FeCl_3 \cdot 6H_2O$ in methanol under argon, leading after precipitation to 0.40 g, 10% yield, of polymer.

(iv) Separate 5-ml aliquots of solution A were treated with (a) 1 ml of 0.1 *M* $ZnCl_2$ in methanol and (b) with 1 ml 0.1 *M* $AlCl_3$ in methanol; 5-ml blanks of acrylonitrile were treated similarly with $ZnCl_2$ and $AlCl_3$ solutions. After 4 hr, the polymer was precipitated and collected, from (a) 0.53 g, 13% yield, from (b) 0.75 g, 19% yield, and from the blanks, none.

(v) Separate 5-ml aliquots of solutions A, B, and C were treated with 1 ml of 0.10 *M* $Fe(NO_3)_3 \cdot 9H_2O$ in methanol under argon. Polymer was collected after 5 hr, (a) 1.0 g, 25% yield; (b) 1.0 g, 25% yield; (c) 1.2 g, 30% yield.

(vi) Separate 5-ml aliquots of solutions B and C were treated with 0.5 ml of concentrated hydrochloric acid in 1 ml of methanol leading to 0.06 g, 1.5% yield, and 0.60 g, 15% yield of polymer, respectively.

Preparation of Polyacrylonitrile. Analysis of Polymers. Polyacrylonitrile was prepared by stirring 5 ml of acrylonitrile, 6.5 ml of water, 3.5 ml of 0.065 *M* aqueous ferrous sulfate, and 2 ml of 30% hydrogen peroxide for 3 hr. The polymer was washed with water,

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(17) R. W. Hoffmann, *Angew. Chem.*, **75**, 168 (1963); *Chem. Ber.*, **97**, 2763 (1964).

(18) S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2845 (1961).

methanol, and petroleum ether and dried under vacuum at 60°. Polymer prepared with hydrogen peroxide as initiator showed an O—H band at 2.85 and a strong $C\equiv N$ band at 4.45 μ.

Polymer prepared with compound I as initiator showed a very weak OH absorption at 2.8–3.0, a very weak C=O band at 6.0, characteristic monosubstituted phenyl band at 13.2 and 14.2, and a strong $C\equiv N$ band at 4.45 μ. The ultraviolet spectrum showed a band at 235 and a broad band at 330–360 mμ. The infrared spectra of polyacrylonitrile prepared with N,N'-dibenzoyldiimide as initiator in both the H^+ and Fe^{3+} series showed an O—H band at 2.8–3.0, a strong C=O band at 5.95, characteristic monosubstituted phenyl bands at 13.2 and 14.4, and the strong $C\equiv N$ band at 4.45 μ. The infrared spectra of polyacrylonitrile prepared with diethyl azodicarboxylate as initiator in both the H^+ and Fe^{3+} series showed O—H band at 2.8–3.0, strong C=O band at 5.78, and the strong $C\equiv N$ band at 4.45 μ. All samples of polymer were extracted with petroleum ether for 48 hr to remove occluded methanol and initiator fragments. Combustion of the polyacrylonitrile formed by the ferric-induced methanolysis of I, N,N'-dibenzoyldiimide, and diethyl azodicarboxylate left no residue.

The Electrolytic Decarboxylation of *cis*- and *trans*-Bicyclo[3.1.0]hexane-3-carboxylic Acids

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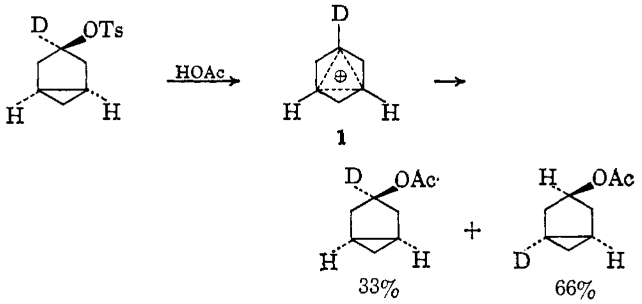
Abstract: The electrolytic oxidative decarboxylation of *cis*- and *trans*-bicyclo[3.1.0]hexane-3-carboxylic acid was investigated. When the electrolysis was run in pyridine–water the predominant products were *cis*- and *trans*-bicyclo[3.1.0]hexan-2-ols. These rearranged alcohols are explained on the basis of cationic intermediates. The reactions are stereospecific insofar as the *trans* acid yields mostly *trans* alcohol while the *cis* acid yields *cis* alcohol as the major product. Bicyclo[3.1.0]hexane-3-carboxylic acid labeled with deuterium at C-6 was converted to bicyclo[3.1.0]hexan-2-ols with no deuterium shift. These results are discussed in relation to the question of the existence of trishomocyclopropenyl cations.

The nature of the 3-bicyclo[3.1.0]hexyl cation has been the topic of numerous recent publications.[2-8] The synthesis of this cation has been approached by three different research groups from three different directions. Winstein and co-workers were the first to investigate the 3-bicyclo[3.1.0]hexyl cation.[2,4,5] They found that acetolysis of both *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonate afforded *cis*-3-bicyclo[3.1.0]hexyl acetate as the major solvolysis product. In addition it was shown that the *cis* toluenesulfonate solvolyzed about ten times faster than the *trans* isomer to give a quantitative yield of *cis* acetate. The *cis* toluenesulfonate showed a "special salt effect" while the *trans* toluenesulfonate failed to act similarly. Finally, Winstein and co-workers investigated the acetolysis of the epimeric 3-deuterio-3-bicyclo[3.1.0]hexyl toluenesulfonates. The *cis* toluenesulfonate yielded *cis* acetate with the deuterium statistically distributed between the 1, 3, and 5 positions while the *trans* toluenesulfonate gave *cis* acetate with no deuterium scrambling. On the basis of these data, Winstein postulated the existence of the unique nonclassical ion (**1**) for which he coined the name "trishomocyclopropenyl cation."



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Corey and Dawson[6] generated a 3-bicyclo[3.1.0]hexyl cation by deamination of the epimeric 3-aminobicyclo[3.1.0]hexanes. Their results differed drastically from those obtained in solvolysis studies. In contrast to Winstein's acetolysis, deamination of either epimer of 3-aminobicyclo[3.1.0]hexane yielded both epimeric 3-alcohols and also both epimeric 2-alcohols (probably *via* a C-2 to C-3 hydride shift). In addition, these workers deaminated 3-deuterio-*cis*-3-aminobicyclo[3.1.0]hexane and found less than 50% deuterium scrambling in the resulting *cis*-3-alcohol. The *trans*-3-alcohol isolated from the same reaction showed no deuterium shift. These results were interpreted as evidence for the absence of a trishomocyclopropenyl cationic intermediate in the deaminations.

A third approach to the 3-bicyclo[3.1.0]hexyl cation was that of Freeman and co-workers.[9] They reasoned that if the trishomocyclopropenyl cation was an unusually stable intermediate, as might be expected, protonation of bicyclo[3.1.0]hex-2-ene (**2**) followed by addition of the nucleophile X might yield **3**. However, they found no evidence for the formation of a trishomocyclopropenyl cation.

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