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Reduction Products in Copper(I)-Promoted Diazonium Ion Reactions. Hydrogen Abstraction from Amines Coordinated to Copper(I), from Water, and from Transient Radicals

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Received November 28, 1973

Reduction products are observed in amine–copper(I) perchlorate promoted decomposition of aryldiazonium salts when the amine ligands are capable of hydrogen atom donation. The effective reducing agents evidently are the complexed rather than the free ligands, *i.e.*, the tris(amine)copper(I) cation in the case of tetra- and tricoordinated salts and the bis(amine)copper(I) cation in the dicoordinated systems. In the presence of excess ligand a new product is obtained, which is probably an ammonium salt formed from the amine and the incipient aryl cation. In the absence of hydrogen-donating ligands it has been shown that the small but consistent amount of benzophenone formed in the copper(I)-promoted decomposition of 2-diazobenzophenone tetrafluoroborate arises from (a) the precursor to 9-fluorenone and (b) the solvent, water. Hydrogen atom abstraction from both these sources is rate determining and subject to a kinetic isotope effect. Since water is a notoriously poor hydrogen atom donor, transfer of a hydrogen atom from the aquated coordination sphere of copper(I) *via* a bridged intermediate is postulated.

In the course of our investigations of copper(I) oxide and copper(I) perchlorate decompositions of aryldiazonium tetrafluoroborates,[2] it was noted that reduction products were consistently produced. A thorough study of the hydrogen source in these decompositions was, therefore, undertaken.

The tetrafluoroborate salt of 2-diazobenzophenone (1) was selected for this purpose because of the large amount of reliable data that were already available. This compound, as are all aromatic diazonium compounds, is capable of cleaving homolytically and/or heterolytically, depending on conditions. The decomposition of 2-diazobenzophenone tetrafluoroborate (1) was first carried out by Graebe and Ullman,[3] who found that 1 could be converted into 9-fluorenone (4). DeTar and Relyea[4] showed the formation of *o*-hydroxybenzophenone (3, Z = OH) along with 9-fluorenone (4) in the system, in the presence and absence of a copper catalyst. Lewin and Cohen[5a] then elucidated conditions under which homolytic and heterolytic cleavage of the carbon–nitrogen bond occurred. They found that thermal decomposition of diazonium salts in acidic solution produced phenyl cations, whereas the room temperature reaction, with a catalyst, led to a phenyl radical. Their proposed mechanism of the copper(I)-catalyzed decomposition of 2-diazobenzophenone tetrafluoroborate seemed to hold for amine–copper(I) perchlorate promoted decompositions with the addition of dimerization of radical A.[2] Thus, it has been shown that good yields of the phenol (3, Z = OH) can be obtained in the presence of a large excess of cupric ion and that benzophenone (2) is produced in the presence of hydrogen donors such as acetone and ethanol.[2] However, benzophenone was formed in both the copper(I) oxide and the amine–copper(I) perchlorate promoted reactions even in the absence of such hydrogen donors. A similar observation had been previously made[5a] and several possible pathways for benzophenone (2) formation were considered in conjunction with the proposed reaction scheme;[5a] the authors concluded, however, that "the nature of the reducing agent remains obscure." See Scheme I.

Results and Discussion

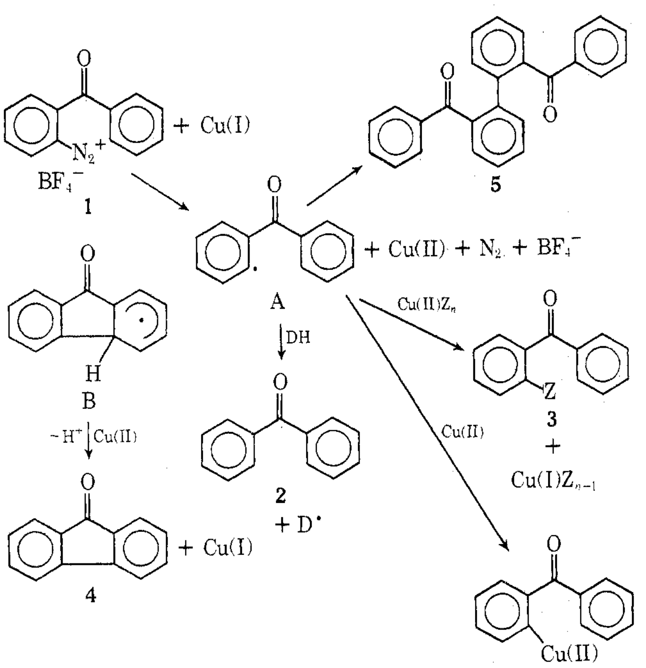
Reduction Products. A. In Amine–Copper(I) Perchlorate Promoted Reactions. Benzophenone (2) was formed in amine–copper(I) perchlorate promoted decom-

Table I
Product Composition in Amine–Copper(I) Perchlorate Promoted Decompositions of 2-Diazobenzophenone Tetrafluoroborate (1)[a]

No.	Catalyst	Product yields, %[b] Benzophenone (2)	2-Hydroxybenzophenone (3)	9-Fluorenone (4)	2,2′-Dibenzoylbiphenyl (5)
1	Tetrakis(pyridine)copper(I) perchlorate	0.8	2.8	28.7	53.0
2	Tetrakis(quinoline)copper(I) perchlorate	*c*	*c*	67.0	10.5
3	Tetrakis(4-picoline)copper(I) perchlorate	7.6	3.7	28.7	31.4
4	Tris(2-picoline)copper(I) perchlorate	1.8	1.1	27.6	76.5
5	Tris(2-ethylpyridine)-copper(I) perchlorate	8.6	1.0	31.5	73.0
6	Bis(2,6-lutidine)copper(I) perchlorate	4.1	0.8	35.0	13.1
7	Bis(γ-collidine)copper(I) perchlorate	10.3	0	87.0	*c*
8	Bis(2-methylquinoline)-copper(I) perchlorate	3.1	0.5	57.1	9.0
9	Bis(8-methylquinoline)-copper(I) perchlorate	7.8	*c*	44.7	8.6

[a] Reaction of 0.6 mmol of 2-diazobenzophenone tetrafluoroborate and 1.0 mmol of catalyst in 30 ml of water. [b] The yields were determined by vpc analysis *vs.* hexadecane as the added internal standard. [c] Present but as less than 1% of the overall reaction.

Scheme I
Homolytic Decomposition Pathway of 2-Diazobenzophenone Tetrafluoroborate[a]



[a] References 2 and 5.

positions of **1**, as shown in Table I.[5b] It was noted that a rough correlation existed between the extent of benzophenone (**2**) formation and the number of methyl groups on the ligating amine of the copper(I) perchlorate. Thus, reactions promoted by tetrakis(pyridine)- and tetrakis(quinoline)copper(I) perchlorate, neither of which have methyl groups (entries 1, 2), gave practically no benzophenone and the reaction promoted by bis (γ-collidine)copper(I) perchlorate, with six methyl groups per mole, gave *ca.* 10% benzophenone (entry 7). In fact, the relative hydrogen atom donating ability of the methyl- and ethylpyridines (entries 4, 5) seems to parallel that of the methyl- and ethylbenzene analogs. Thus, it is known that the hydrogen donating ability of ethylbenzene toward phenyl radicals is 3 times greater than that of toluene.[6] Similarly, the data in Table I suggest that the hydrogen-donating ability of tris(2-ethylpyridine)copper(I) perchlorate is 4.8 times greater than that of tris(2-picoline)copper(I) perchlorate toward the benzophenone radical.[7] On the other hand, the considerably lower yield of benzophenone obtained when the reaction was promoted by tris(2-picoline)copper(I) perchlorate as compared to tetrakis(4-picoline)copper(I) perchlorate is in striking contrast to the somewhat greater hydrogen-donating ability reported for 2-picoline *vs.* 4-picoline.[8]

In addition, it was noted that whenever relatively large yields of benzophenone were formed, high-boiling, basic materials were also produced. These were expected to be heterocyclic-amine disubstituted ethanes arising from the dimerization of the radicals formed by hydrogen abstraction. In fact, the high-boiling base produced in the tris(2-picoline)copper(I) perchlorate promoted reaction of **1** was separated and shown to be 1,2-di(2-pyridyl)ethane by comparison with an authentic sample.[9]

Increased yields of reduction product **2** were also observed with the addition of excess heterocyclic amine ligand to the reaction mixture (Table II) and a rough correlation can be seen between the yield of benzophenone and the number of moles of methyl groups in each system.

Two major differences are seen between reduction by substituted pyridines and the hydrogen donor dioxane. Whereas the addition of the hydrogen donor dioxane leads to increasing yields of benzophenone, tending asymptotically to 100% conversion,[10] none of the substituted pyridines exhibited such behavior. In fact, some of the amines lead to a broad maximum in the yield of benzophenone with higher amine concentrations. In addition, the effectiveness of the heterocyclic amines as reducing agents is not as expected.

The extent of reduction was expected to be relatively independent of the position of the methyl substituent on the pyridine ring, since the hydrogen-donating abilities of 2- and 4-picoline are known to be essentially the same[8] and γ-collidine is 3 times as effective as 4-picoline,[6] by virtue of having three methyl groups. It was observed that this in-

Table II
Product Composition as a Function of Excess Ligand in Amine–Copper(I) Perchlorate Promoted Decompositions of 2-Diazobenzophenone Tetrafluoroborate (1)[a]

Catalyst (registry no.)	Added ligand,[b] mmol	Total methyl[c] groups, mmol	Product yield, %[d]				
			Benzophenone (2)	2-Hydroxybenzophenone (3)	9-Fluorenone (4)	2,2′-Dibenzoylbiphenyl (5)	Total
Tetrakis(pyridine)copper(I) perchlorate (21465-66-7)	0	0	0.8	2.8	28.7	53.0	85.3
	3	0	*e*	0.6	40.3	56.0	96.9
	30	0	*e*	*e*	25.4	40.5	65.9
Tetrakis(quinoline)copper(I) perchlorate (52019-93-9)	0	0	*e*	*e*	67.0	10.5	77.5
	3	0	*e*	*e*	47.2	64.0	111.2
Tetrakis(4-picoline)copper(I) perchlorate (35232-25-8)	0	4	7.6	3.7	28.7	31.4	71.4
	2	6	15.4	2.5	27.1	0	45.0
	3	7	18.0	2.3	22.4	*f*	*f*
	4	8	21.3	2.3	18.5	*f*	*f*
	10	14	24.4	2.8	1.8	*f*	*f*
Tris(2-picoline)copper(I) perchlorate (37834-33-6)	0	3	1.8	1.1	27.6	76.5	107.0
	1.5	4.5	3.0	21.8	11.1	*f*	*f*
	5	8	4.4	27.4	6.1	*f*	*f*
	7	10	6.0	25.4	6.0	*f*	*f*
	11	14	9.1	22.6	7.3	*f*	*f*
	17	20	10.6	22.2	4.3	*f*	*f*
Tris(2-ethylpyridine)copper(I) perchlorate (37834-25-6)	0	3	8.6	1.0	31.5	73.0	113.1
	3	6	19.0	*e*	7.3	*f*	*f*
	6	9	15.5	6.0	*e*	*f*	*f*
Bis(2-methylquinoline)copper(I) perchlorate (51933-28-9)	0	2	3.1	0.5	57.1	9.0	69.7
	3	5	14.3	31.1	3.7	32.2	71.3
Bis(8-methylquinoline)copper(I) perchlorate (51933-30-3)	0	2	7.8	*e*	44.7	8.6	61.1
	3	5	12.7	6.2	5.5	72.0	96.4
Bis(2,6-lutidine)copper(I) perchlorate (51933-32-5)	0	4	4.1	0.8	35.0	13.1	52.2
	0.5	5	9.0	*e*	42.5	32.8	84.3
	1	6	11.3	*e*	26.2	*f*	*f*
	2	8	15.0	*e*	31.7	*f*	*f*
	3.5	11	22.5	*e*	20.4	4.0	46.9
	7	18	23.4	*e*	15.6	*f*	*f*
	9	22	28.6	1.8	9.2	*f*	*f*
	11	26	18.2	1.3	7.2	*f*	*f*
Bis(γ-collidine)copper(I) perchlorate (51933-34-7)	0	6	10.3	0	87.0	*e*	97.3
	0.3	7	12.8	*e*	33.4	24.0	70.2
	2	12	27.7	*e*	12.2	5.7	45.6
	2.6	14	31.5	*e*	10.0	3.5	46.0
	3.5	16.5	30.8	*e*	2.7	*f*	*f*
	5.3	22	25.3	1.6	0.9	16.0	43.8

[a] Reaction of 0.6 mmol of 2-diazobenzophenone tetrafluoroborate and 1.0 mmol of catalyst in 30 ml of water. [b] The ligand corresponds to that in the catalyst. [c] Sum of the millimoles of methyl groups from the added excess ligand and from the catalyst. [d] The yields were determined by vpc analysis *vs.* hexadecane as the added internal standard. [e] Present but less than 1% of the overall product. [f] Not determined.

deed was the case when the amount of benzophenone formed in reactions with similar methyl group concentrations was compared for 4-picoline, 2,6-lutidine, and γ-collidine. The results for 2-picoline are, however, in striking disagreement with expectation and with those obtained for other substituted pyridines. The extremely low yields of benzophenone obtained with excess 2-picoline cannot be accounted for by the change in the position of the methyl substituent on the pyridine ring from para to ortho, since such an explanation would be inconsistent with the observed results for benzophenone formation from the copper(I) complexes of 2,6-lutidine and γ-collidine.

It thus appears that the copper catalyst plays a significant role in the reducing ability of the excess ligand. In order to understand such a role we considered the possible dissociation of the copper(I) complexes in the reaction medium.

The formation constants for tetrakis(4-picoline)copper(I) and tris(2-picoline)copper(I) have been reported[11] and we have calculated the equilibrium concentrations of the various species present, starting with known amounts of total ligand and total metal and solving the equations for equilibrium numerically.[12] The results of these calculations in each case implicate the tricoordinated species, as an important reducing agent, for the yield of benzophenone follows the concentration of that species (Appendix). However, the reducing ability of tris(4-picoline)copper(I) appears to substantially exceed that of tris(2-picoline)copper(I). Thus, a concentration of 5×10^{-3} *M* tricoordinated copper(I) leads to the production of 7.4% benzophenone with 4-picoline as the ligand but to only 1.8% benzophenone when 2-picoline is used (Table II). In view of the known structure of *tris(2-picoline)copper(I) perchlorate*[13] it is tempting to suggest that possibly only one of the three methyl groups in this cation is available as a hydrogen donor, the other two being sterically inaccessible to the relatively bulky benzophenone radical, A. This situation would not obtain in the tris(4-picoline)copper(I) ion, since the methyl groups would be peripherally accessible, independent of whether copper(I) had trigonal or tetrahedral bonding.

No formation constants are available for bis(γ-collidine)copper(I) or for bis(2,6-lutidine)copper(I). These may be estimated using the relationship $\log K_1 = a\mathrm{p}K_a + b$

Table III
Product Composition in the Copper(I) Oxide Promoted Decomposition of 2-Diazobenzophenone Tetrafluoroborate (1)[a]

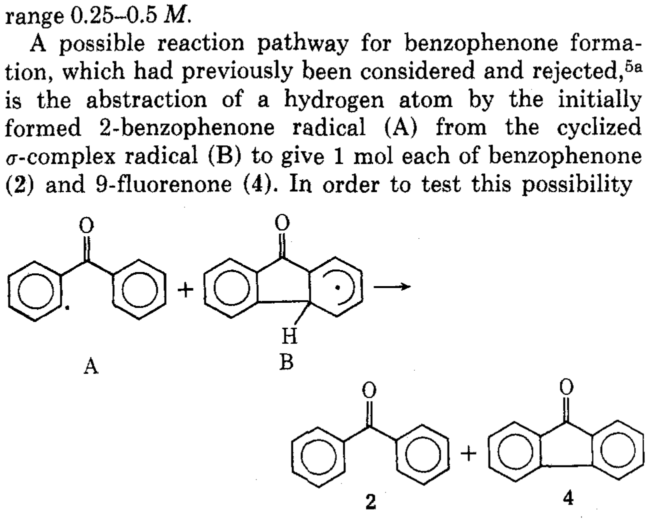
Molarity of H_2SO_4	Product yields, %[b,c] Benzophenone (2)	2-Hydroxybenzophenone (3)	9-Fluorenone (4)
0.25	11.4	*d*	51.4
0.38	14.3	*d*	44.5
0.50	22.7	*d*	38.4
0.63	2.1	*d*	49.1
0.75	3.2	*d*	51.3
1.50	3.1	*d*	60.5

[a] Reaction of 0.6 mmol of 2-diazobenzophenone tetrafluoroborate and 0.42 mmol of copper(I) oxide (99+% pure) in 30 ml of aqueous H_2SO_4. [b] The yields were determined by vpc analysis *vs.* hexadecane as the added internal standard. [c] The balance of the reaction was 2,2′-dibenzoylbiphenyl; overall yields were 95–100%. [d] Present but less than 1% of the overall reaction.

where *a* and *b* are constants;[14] the approximate relationship K_1/K_2 = constant can then lead to an estimate of K_2. Using these approximations we calculated values of $K_1 = 1 \times 10^6$ for 2,6-lutidine and 8.7×10^6 for γ-collidine; $K_2 = 7 \times 10^2$ for 2,6-lutidine and 6.2×10^3 for γ-collidine. Concentrations of free metal, free ligand, and monoligated and diligated copper(I) were then calculated using these values and the total metal and total ligand concentrations used in each experimental run. The results, although approximate, implicate the dicoordinated copper cation and account for the leveling off observed for the yield of benzophenone. At total ligand concentrations above 0.13 *M* all the metal is essentially dicoordinated; thus the concentration of the reducing agent is constant and consequently the extent of benzophenone formation remains at its maximum.

B. In Copper(I) Oxide Promoted Reactions. A small, but persistent, amount of benzophenone (2) was consistently formed in the copper(I) oxide promoted decomposition of 1 in acid medium. In this investigation, ultrapure (99+%) copper(I) oxide was used, and although no pH effect on the product composition had been observed when amine–copper(I) perchlorates[2] or partially (20%) oxidized copper(I) oxide had been used,[15] a rather striking relationship between benzophenone formation and acidity was noted (Table III).[16] All further experiments were conducted at accurately determined sulfuric acid concentrations in the range 0.25–0.5 *M*.

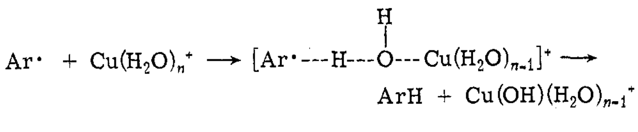
A possible reaction pathway for benzophenone formation, which had previously been considered and rejected,[5a] is the abstraction of a hydrogen atom by the initially formed 2-benzophenone radical (A) from the cyclized σ-complex radical (B) to give 1 mol each of benzophenone (2) and 9-fluorenone (4). In order to test this possibility



2,3,4,5,6-pentadeuterio-2′-diazobenzophenone tetrafluoroborate (1-d_5) was prepared and subjected to copper(I) oxide promoted decomposition. The results (Table IV) show that, as expected, essentially the same product composition is obtained using pentadeuterated or nondeuterated diazonium salts. The actual yield of hexadeuterated benzophenone (2-d_6) (determined by mass spectrometry) was on the order of 2% of the overall yield in each case. The proposed pathway, involving the collision of two transient radicals, therefore accounts for *ca.* 20% of the benzophenone in 0.25 *M* H_2SO_4 and for *ca.* 10% of the benzophenone in 0.5 *M* H_2SO_4.

The involvement of water as a hydrogen source, either directly or *via* abstraction from 2-hydroxybenzophenone (3), had also been considered; it had been rejected because no deuterium-containing benzophenone was obtained when the reaction was conducted in D_2O.[5] Under our reaction conditions, however, 10% of the benzophenone was monodeuterated when the copper(I) oxide promoted decomposition of 1 was carried out in 0.5 *M* D_2SO_4–D_2O solution (Table V).[17] This deuteration pathway must involve water directly because no *o*-hydroxybenzophenone (3) is obtained in any of these reactions. Since homolytic cleavage of the H–O–H bond with subsequent addition to a carbon atom is an energetically unfavorable process,[19] reduction may involve the hydrolysis of an organocopper. It has been demonstrated that arylcoppers are produced in copper-promoted aryldiazonium ion decompositions[20] and this possibility would also be consistent with the observed formation of 2,2′-dibenzoylbiphenyl,[2] which is an expected product from an arylcopper.[21] On the other hand, rather special conditions are required for the production of arylcoppers from diazonium ions[20] and therefore an alternative pathway should be considered.

In order to avoid the formation of the high-energy species OH·, a hydrogen atom may be transferred from the aquated coordination sphere of the copper(I) ion to the benzophenone radical (A) *via* a bridged intermediate. Such hydrogen atom transfers are weldocumented in reactions between inorganic ions.[22]


$$\mathrm{Ar}\cdot + \mathrm{Cu(H_2O)}_n^+ \longrightarrow [\mathrm{Ar}\cdot\text{---}\mathrm{H}\text{---}\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}\text{---}\mathrm{Cu(H_2O)}_{n-1}]^+ \longrightarrow \mathrm{ArH} + \mathrm{Cu(OH)(H_2O)}_{n-1}^+$$

Since the two hydrogen sources identified so far, namely, H abstraction from a cyclized radical B and from water, apparently account for a maximum of 30% of the benzophenone formed, and since no other hydrogen sources seemed to be available, the possible operation of an isotope effect was considered. Thus, if an isotope effect were present in the hydrogen atom abstraction *via* each pathway and if the pathways were of comparable energy, isotopic substitution in either case would divert the reaction to the alternative path. The results of carrying out the decomposition of pentadeuteriodiazobenzophenone tetrafluoroborate (1-d_5) in 0.5 *M* D_2SO_4–D_2O support this hypothesis; the overall yield of benzophenone was 14.5% and 87% of it was hexadeuterated.

Assessment of the magnitude of the deuterium isotope effects in these steps is rather difficult. There are no reported values for the isotope effect associated with the abstraction of a hydrogen atom from the aquation sphere of metal ions. The deuterium isotope effect for the abstraction of a hydrogen atom from phenol has been reported to be 1.32.[23] If a calculation is carried out using this value for the scission of the O–H bond, a value of 2.3 is obtained for k_H/k_D in the hydrogen abstraction from B (see Appendix for calculation). This value is lower than that of 4, commonly associated with isotope effects in C–H bond breaking by an aryl radical.[6] However, B is a reactive intermedi-

Table IV
Product Composition and Extent of Deuteration in the Copper(I) Oxide Promoted Reaction of Pentadeuterated 2-Diazobenzophenone Tetrafluoroborate (1-d_5)[a]

Diazonium tetrafluoroborate	Conditions	Product yields, %[b,c] Benzophenone (2)	2-Hydroxybenzophenone (3)	9-Fluorenone (4)	% deuteration of benzophenone d_5[f]	d_6[g]
1[d]	0.5 N H_2SO_4	11.4	e	51.4		
1-d_5[h]	0.5 N H_2SO_4	11.4	1.0	43.2	81.4	18.6
1[d]	1.0 N H_2SO_4	22.7	e	38.4		
1-d_5[h]	1.0 N H_2SO_4	20.9	e	30.0	91.3	8.7

[a] Reaction of 0.6 mmol of diazonium tetrafluoroborate and 0.42 mmol of copper(I) oxide (99+% pure) in 30 ml volume. [b] The yields were determined by vpc analysis *vs.* hexadecane as the added internal standard. [c] The balance of the reaction was 2,2′-dibenzoylbiphenyl; overall yields were 85–100%. [d] 2-Diazobenzophenone tetrafluoroborate. [e] Present but less than 1% of the overall reaction. [f] 2,3,4,5,6-Pentadeuteriobenzophenone. [g] 2,2′,3,4,5,6-Hexadeuteriobenzophenone. [h] 2,3,4,5,6-Pentadeuterio-2′-diazobenzophenone tetrafluoroborate.

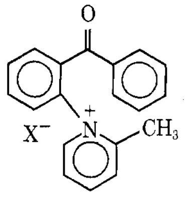
Table V
Decomposition of Undeuterated and Pentadeuterated 2-Diazobenzophenone Tetrafluoroborate (1 and 1-d_5) in Heavy Water[a]

No.	Diazonium tetrafluoroborate	Conditions	Product yields, %[b,c] Benzophenone (2)	2-Hydroxybenzophenone (3)	9-Fluorenone (4)	% deuteration of benzophenone d_0[f]	d_1[g]
1	1[d]	1.0 N D_2SO_4–D_2O	11.9	e	46.5	89.3	10.7
2	1[d]	1.0 N H_2SO_4–H_2O	22.7	e	38.4		
						d_5[i]	d_6[j]
3	1-d_5[h]	1.0 N H_2SO_4–H_2O	20.9	e	30.0	91.3	8.7
4	1-d_5[h]	1.0 N H_2SO_4–25% D_2O				84.0	16.0
5	1-d_5[h]	1.0 N H_2SO_4–50% D_2O	11.5	e	46.4	68.6	31.4
6	1-d_5[h]	1.0 N H_2SO_4–75% D_2O				56.0	44.0
7	1-d_5[h]	1.0 N D_2SO_4–100% D_2O	14.5	e	43.8	13.0	87.0

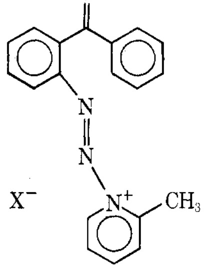
[a] Reaction of 0.6 mmol of 2-diazonium tetrafluoroborate and 0.42 mmol of copper(I) oxide (99+% pure) in 30 ml volume. [b] The yields were determined by vpc analysis *vs.* hexadecane as the added internal standard. [c] The balance of the reaction was 2,2′-dibenzoylbiphenyl; overall yields were 85–100%. [d] 2-Diazobenophenone tetrafluoroborate. [e] Present but less than 1% of the overall reaction. [f] Undeuterated benzophenone. [g] 2-Deuteriobenzophenone. [h] 2,3,4,5,6-Pentadeuterio-2′-diazobenzophenone tetrafluoroborate. [i] 2,3,4,5,6-Pentadeuteriobenzophenone. [j] 2,2′,3,4,5,6-Hexadeuteriobenzophenone.

ate with excess energy and may therefore suffer a smaller isotope effect. In fact, abstraction of a hydrogen atom from B is somewhat analogous to the dehydrogenation of an arylcyclohexadienyl radical in free-radical arylation reactions and can thus be assumed to be rather small.[24] In the extreme case, there might be no isotope effect on this step ($k_H/k_D = 1$). If this assumption is made, an isotope effect of *ca.* 3 is obtained for the abstraction of a hydrogen atom from the aquation sphere of Cu(I) (see Appendix for calculation). It should be emphasized that both sets of values for the isotope effects are extremely rough. However, the last set ($k_H/k_D = 1$ for abstraction from B and $k_H/k_D = 3$ for abstraction from water) is more consistent with the results in Table V. Thus, the small decrease in the yield of 2 in the reaction of 1-d_5 as compared with 1 (no. 2 and 3) supports a very small kinetic isotope effect for abstraction from B. The changes in the yield of 2 due to reaction in deuterated solvent are more difficult to relate to the primary isotope effect, owing to the possible operation of secondary and solvent isotope effects and differences in pH. It is clear, however, that the results are in the right direction, since the observed decrease in benzophenone (2) production (no. 1 *vs.* 2 and 4 *vs.* 7) cannot be associated with decreased acidity (Table III) and suggests a kinetic isotope effect >1.

Formation of an Unresolved Product. In the course of the amine–copper(I) perchlorate promoted decompositions, it was noted that the total product yields decreased strikingly with added amine. Since all the components in the organic layer were identified (as **2, 3, 4,** and **5**), it was postulated that a water-soluble material must comprise the balance of the product. In view of the unknown material's water solubility, it was assumed to be ionic and since its formation seemed to depend on the presence of excess 2-picoline, two possibilities could be those shown below. The



6a



6b

phenyl analog of **6a** has been postulated by Nesmeyanov[25] and the phenyl analog of **6b** by Abramovitch;[26] however, in neither case were the compounds actually isolated from the decomposition of a diazonium salt.

In order to distinguish between the postulated structures **6a** and **6b**, nitrogen evolution measurements were taken.[27] The total organic products only accounted for 52.8% of the starting material when the tris(2-picoline)copper(I) perchlorate promoted reaction of 1 was carried out in the presence of 3 mmol excess 2-picoline; in the absence of 2-picoline the total of recovered organic products was essentially 100%. If, therefore, structure **6b** were formed, the reaction in the presence of excess 2-picoline should evolve only one-half the moles of nitrogen that would be evolved in the same reaction in the absence of excess 2-picoline. The results of nitrogen evolution measurements in the reaction of

0.6 mmol of 2-diazobenzophenone tetrafluoroborate (**1**) with 1.0 mmol of tris(2-picoline)copper(I) perchlorate in 30 ml of water in the presence of 3.0 mmol of 2-picoline (0.58 mmol of nitrogen) were the same as those without the added 2-picoline (0.61 mmol of nitrogen) and both are in excellent agreement with the calculated amount of nitrogen that should have been evolved (0.60 mmol). Since nitrogen evolution from the diazonium salt was quantitative under conditions where the organic products accounted for only 52.8% of the product and since structure **6b** should retain nitrogen, it was concluded that **6b** was most probably not the structure of the salt formed.

The reaction in the presence of excess 2-picoline was repeated. The organic products were removed by extraction with methylene chloride and the copper salts were precipitated by dioxane and removed by filtration. The solvent was then evaporated, leaving an oil which showed intense infrared absorptions around 1100 cm^{-1} (BF_4^- and ClO_4^-) along with strong bands at 1640 and 1740 cm^{-1}. Inasmuch as the carbonyl absorption of benzophenone is at 1650 cm$^-$ structure **6a** for this oil was possible.

A dinitrophenylhydrazone (DNPH) derivative of the oil was prepared and the infrared spectrum was taken and compared with that of the DNPH derivative of authentic benzophenone. The derivative of the unknown no longer exhibited absorptions in the 1100-cm^{-1} region or at 1740 cm^{-1}. Its infrared spectrum differed from that of the DNPH of benzophenone only in that two bands, at 1140 and 1370 cm^{-1}, attributable to 2-picoline, were present. The absence of the bands due to tetrafluoroborate or perchlorate anion may be due to exchange with chloride ion during preparation of the DNPH derivative. Alternatively, arylation of the 2-picoline may have occurred during derivatization, along the lines proposed by Abramovitch.[26]

If indeed an ammonium salt like **6a** is formed in the presence of excess 2-picoline, it might account for the significant yield of 2-hydroxybenzophenone (**3**) observed in these reactions. It might well be that such a salt would be slowly decomposed by water to give the phenol.

The reasons for the extensive formation of the ammonium salt in reactions with 2-picoline is not known. Possibly the rather serious steric congestion in the tris(amine)copper(I) salts retards the copper(I)-promoted decomposition sufficiently to allow competing reactions of this type to become important.

Conclusions

The use of ligands capable of hydrogen atom donation in amine–copper(I) perchlorate promoted aryldiazonium ion decompositions leads to the formation of reduction products. The effective hydrogen donor is evidently the triligated copper(I) cation for the tetra- and tricoordinated complexes and the diligated species for the dicoordinated complexes. In the presence of excess ligand a relatively stable ammonium salt is formed, apparently by attack of the amine on the incipient aryl cation.

Therefore, the complexes of choice for carrying out copper(I)-promoted aryldiazonium salt decompositions in neutral water are tetrakis(pyridine)- and tetrakis(quinoline)copper(I) perchlorate with no excess ligand present.

In strong acid, reduction products can be formed by H atom transfer from the aquated coordination sphere of copper(I) *via* a bridged intermediate.

Experimental Section

Physical Measurements. Infrared spectra in the wavenumber range 4000–600 cm^{-1} were obtained with a Perkin-Elmer Model 521 spectrophotometer using potassium bromide pellets.

pH measurements were read with a Beckman Model 76 expanded-scale pH meter. The meter was standardized with buffer solutions.

Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 mass spectrometer. For determinations of deuterium incorporation the spectra at 16 eV were recorded on the strip chart. For undeuterated materials the agreement between the experimental value of the (M + 1) peak and the value calculated from natural isotopic abundances was better than 1%.

Gas chromatographic analysis was performed as described previously.[2]

Preparation and Decomposition of 2-Diazobenzophenone Tetrafluoroborate. The procedures followed were as previously described.[2]

Copper(I) Oxide. The material designated 99+% pure (Alfa Inorganics) was kept in a nitrogen-filled drybox until used.

Amine–Copper (I) Perchlorates. The preparation of these salts has been described previously.[28]

Nitrogen Evolution Measurements. The procedure described by Siggia for nitrogen measurement was followed.[27]

The nitrogen evolved from the following reactions was measured: reaction 1, 0.6 mmol of 2-diazobenzophenone tetrafluoroborate and 1.0 mmol of tris(2-picoline)copper(I) perchlorate in 30 ml of water; reaction 2, 0.6 mmol of 2-diazobenzophenone tetrafluoroborate with 3 mmol of 2-picoline and 1.0 mmol of tris(2-picoline)copper(I)perchlorate in 30 ml of water.

First two control reactions were run.

A stirred solution of diazonium salt with (or without) 2-picoline in a flask equipped with a solid addition funnel for the copper(I) catalyst was connected to a 100-ml nitrogen measurement apparatus (nitrometer) containing a 50% potassium hydroxide solution (71.5 g of potassium hydroxide per 100 ml of water). Carbon dioxide was passed through the apparatus to flush out the air; it was continuously passed through until the bubbles reached a minimum size in the nitrometer. A blank was run on the carbon dioxide to correct the volume readings for the diazonium salt for a given time interval.

In an actual determination, the air was swept out of the apparatus. The inert gas was removed from the nitrometer and tris(2-picoline)copper(I) perchlorate was added to the solution of 2-diazobenzophenone tetrafluoroborate with (or without) 2-picoline, and the time was noted. The reaction mixture was stirred for 15 min. The carbon dioxide flow was continued throughout this period. The volume of the gas collected was read, the leveling bulb on the nitrometer being used to set the pressure of the gas in the nitrometer equal to atmospheric pressure. The temperature, barometric pressure, and time were noted. The volume of gas collected was corrected for the blank determination made on carbon dioxide. The volume was also corrected for the vapor pressure of the potassium hydroxide solution.

The volume of nitrogen collected was 25.2 ml for reaction 1 and 23.0 ml for reaction 2. The corresponding carbon dioxide blanks were 5.3 and 4.4 ml.

The calculation of the moles of nitrogen collected was as follows. The volume was corrected by subtracting out the CO_2 volume and the pressure was corrected by subtracting out the vapor pressure of 50% aqueous KOH. The volume was then corrected to STP and the number of moles of nitrogen was calculated: reaction 1 gave 0.61 mol of nitrogen; reaction 2 gave 0.58 mol of nitrogen.

Attempted Characterization of an Unresolved Product. The tris(2-picoline)copper(I) perchlorate promoted decomposition of 2-diazobenzophenone tetrafluoroborate in the presence of excess 2-picoline was carried out by the usual procedure.[2] The solution was extracted three times with 150 ml of methylene chloride. To the aqueous layer was then added *ca.* 50 ml of dioxane, whereupon a light blue precipitate formed. The solution was filtered and then evaporated carefully to a few milliliters. Addition of a small volume of CCl_4 caused the separation of an oil, which was separated and placed in a vacuum oven overnight at 105°. An infrared spectrum of the oil showed strong bands at 1740, 1640, and 1100 cm^{-1}.

In a separate isolation experiment the oil was subjected to DNPH derivation.[29] The resulting solid had mp 124°. The infrared spectrum indicated no BF bands.

2,3,4,5,6-Pentadeuterio-2′-aminobenzophenone. A modification of of the procedure employed by Huisgen and Zahler[30] for the preparation of 2-(*o*-aminobenzoyl)naphthalene was used.

To 3 g (0.12 g-atom) of Mg wire in 10 ml of anhydrous ether, 15.2 (0.097 mol) of bromobenzene-d_5 (Norell Chemical) in 100 ml of ether was added dropwise over a period of 1 hr. After an additional 1 hr the Grignard reaction was allowed to cool to room temperature.

The phenylmagnesium bromide-d_5 was then filtered through glass wool to remove the unreacted magnesium wire and added dropwise over a period of 1 hr to a solution of 15.6 g (0.097 mol) of acetylanthranil[31] in 150 ml of ether at 0°. After the solution was evaporated to *ca.* 20 ml, 150 ml of ethanol and 40 ml of concentrated hydrochloric acid were added and the mixture was refluxed for 2 hr. The water layer was then neutralized with concentrated ammonium hydroxide, whereupon yellow crystals of 2-aminobenzoyl-d_5-benzene appeared. The material was recrystallized from hot ethanol, mp 107° (reported for 2-aminobenzophenone, mp 106–110°).[33]

1,2-Di(2-pyridyl)ethane. The procedure of Campbell and Teague was followed to yield 20% of a solid, mp 49–50° (reported mp 49.5–50.5°).[9]

Acknowledgment. One of us (A.H.L.) gratefully acknowledges helpful discussions with Professor I. A. Cohen.

Appendix

Numerical Solution of the Simultaneous Equations for Formation of Metal Complexes. The formation reactions can be written

$$\mathrm{M} + \mathrm{L} \overset{\beta_1}{\rightleftharpoons} \mathrm{ML}$$
$$\mathrm{M} + 2\mathrm{L} \overset{\beta_2}{\rightleftharpoons} \mathrm{ML}_2$$
$$\mathrm{M} + n\mathrm{L} \overset{\beta_n}{\rightleftharpoons} \mathrm{ML}_n$$

with associated formation constants

$$\beta_i = (\mathrm{ML})/(\mathrm{M})(\mathrm{L})^i \qquad (1)$$

The associated equations for conservation of mass are

$$(\mathrm{M})_\mathrm{T} = (\mathrm{M}) + (\mathrm{ML}) + (\mathrm{ML}_2) + \ldots + (\mathrm{ML}_n) \qquad (2)$$

and

$$(\mathrm{L})_\mathrm{T} = (\mathrm{L}) + (\mathrm{ML}) + 2(\mathrm{ML})_2 + \ldots + n(\mathrm{ML}_n) \qquad (3)$$

By combining the equilibrium equations with the conservation equations a single equation in (L) is obtained.

$$0 = -(\mathrm{L})_\mathrm{T} + (\mathrm{L}) + (\mathrm{M})_\mathrm{T}\frac{\beta_1(\mathrm{L}) + 2\beta_2(\mathrm{L})^2 + 3\beta_3(\mathrm{L})^3 + 4\beta_4(\mathrm{L})^4}{1 + \beta_1(\mathrm{L}) + \beta_2(\mathrm{L})^2 + \beta_3(\mathrm{L})^3 + \beta_4(\mathrm{L})^4} \qquad (4)$$

A numerical solution to eq 4 was obtained using an algorithm based on Newton's approximation.[34] The solution was required to satisfy eq 4 within an amount $(\mathrm{L})_\mathrm{T}/10^5$. For the iterative algorithm to converge to a solution a careful choice of an initial approximation for (L) is required. The following choices were found suitable.

If the ligand is present in stoichiometric amounts or more, then take

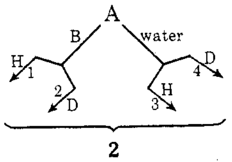
$$(\mathrm{L})_{\text{initial}} = (\mathrm{L})_\mathrm{T} - N(\mathrm{M})_\mathrm{T}$$

otherwise take

$$(\mathrm{L})_{\text{initial}} = (\mathrm{L})_\mathrm{T}/500$$

With these choices a numerical solution was obtained in all cases for less than 20 iterations. It was verified that the solution was independent of the $(\mathrm{L})_{\text{initial}}$ for all cases where the algorithm converged.

Calculation of Isotope Effects. Consider the formation of **2** *via* pathways 1–4. The rate law for the formation of **2** by reaction with B is



2

$$\frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}]$$

The rate law for the formation of **2** by reaction with water is

$$\frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{aq}]^n$$

In the reaction of **1** in protiated water (no. 2 in Table V) **2** is formed according to the expression

$$\frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = k_1[\mathrm{A}][\mathrm{B}] + k_3[\mathrm{A}][\mathrm{aq}]^n \qquad (\mathrm{i})$$

The formation of **2**-d_6 in the reaction of **1**-d_5 (no. 3) in protiated water is

$$\frac{\mathrm{d}[\mathbf{2}\text{-}d_6]}{\mathrm{d}t} = k_2[\mathrm{A}][\mathrm{B}] \qquad (\mathrm{ii})$$

The formation of **2**-d_1 in the reaction of **1** (no. 1) in deuterated water is

$$\frac{\mathrm{d}[\mathbf{2}\text{-}d_1]}{\mathrm{d}t} = k_4[\mathrm{A}][\mathrm{aq}]^n \qquad (\mathrm{iii})$$

Combining ii and iii

$$\frac{\mathrm{d}[\mathbf{2}\text{-}d_6]}{\mathrm{d}[\mathbf{2}\text{-}d_1]} = \frac{k_2[\mathrm{B}]}{k_4[\mathrm{aq}]^n}$$

$$\frac{k_2[\mathrm{B}]}{k_4[\mathrm{aq}]^n} = \frac{\text{yield of } \mathbf{2}\text{-}d_6}{\text{yield of } \mathbf{2}\text{-}d_1} = \frac{1.8}{1.3} = 1.4$$

$$k_2[\mathrm{B}] = 1.4k_4[\mathrm{aq}]^n \qquad (\mathrm{iv})$$

In the reaction of **1**-d_5 in deuterated water (no. 7) **2**-d_6 is formed according to

$$\frac{\mathrm{d}[\mathbf{2}\text{-}d_6]}{\mathrm{d}t} = k_2[\mathrm{A}][\mathrm{B}] + k_4[\mathrm{A}][\mathrm{aq}]^n \qquad (\mathrm{v})$$

Combining iv and v

$$\frac{\mathrm{d}[\mathbf{2}\text{-}d_6]}{\mathrm{d}t} = 2.4k_4[\mathrm{A}][\mathrm{aq}]^n$$

$$2.4k_4[\mathrm{A}][\mathrm{aq}]^n = \text{yield of } \mathbf{2}\text{-}d_6 = 14.5 \times 87 = 12.6$$

$$k_4[\mathrm{A}][\mathrm{aq}]^n = \frac{12.6}{2.4} = 5.3$$

$$k_2[\mathrm{A}][\mathrm{B}] = 12.6 - 5.3 = 7.3$$

Defining

$$\frac{k_1}{k_2} = a = \text{isotope effect on abstraction from B}$$

$$\frac{k_3}{k_4} = b = \text{isotope effect on abstraction from aq}$$

expression i becomes

$$ak_2[\mathrm{A}][\mathrm{B}] + bk_4[\mathrm{A}][\mathrm{aq}]^n = \frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = \text{yield of } \mathbf{2} = 22.7$$

$$7.3a + 5.3b = 22.7$$

Table VI
Calculated Equilibrium Concentrations *vs.* Benzophenone Yield for Tetrakis(4-picoline)copper(I) Perchlorate, L_4CuClO_4[a,b]

Concn, *M*								Yield of benzophenone
Total ligand × 10^2	Total metal × 10^2	Free ligand × 10^2	Free metal × 10^9	LCu × 10^4	L_2Cu × 10^2	L_3Cu × 10^3	L_4Cu × 10^3	(**2**), %[c]
12.0	3.00	5.43	27.8	6.80	2.36	5.00	0.705	7.4
18.6	3.00	11.3	5.15	2.62	1.89	8.35	2.45	15.4
22.0	3.00	14.4	2.83	1.83	1.69	9.44	3.53	18.0
25.0	3.00	17.1	1.81	1.39	1.52	10.1	4.51	21.3
46.0	3.00	36.7	0.203	0.336	0.789	11.3	10.8	24.4

[a] Reference 12. [b] Equilibrium constants used were[11] $[CuL]/[Cu][L] = 4.5 \times 10^5$, $[CuL_2]/[Cu][L] = 6.4 \times 10^2$, $[CuL_3]/[CuL_2][L] = 3.9$, $[CuL_4]/[CuL_3][L] = 2.6$. [c] Determined by vpc analysis *vs.* hexadecane as the added internal standard.

Table VII
Calculated Equilibrium Concentrations *vs.* Benzophenone Yield for Tris(2-picoline)copper(I) Perchlorate, L_3CuClO_4[a,b]

Concn, *M*							Yield of benzophenone
Total ligand × 10^2	Total metal × 10^2	Free ligand × 10^2	Free metal × 10^9	LCu × 10^4	L_2Cu × 10^2	L_3Cu × 10^3	(**2**), %[c]
9.00	3.00	2.96	54.6	40.4	2.15	4.45	1.8
14.0	3.00	7.19	81.6	14.7	1.90	9.55	3.0
25.0	3.00	17.4	9.76	4.25	1.33	16.3	4.4
32.0	3.00	24.2	4.21	2.54	1.11	18.7	6.0
45.0	3.00	36.9	1.37	1.26	0.835	21.5	9.1
65.0	3.00	56.6	0.418	0.592	0.603	23.9	10.6

[a] Reference 12. [b] Equilibrium constants used were[11] $[CuL]/[Cu][L] = 2.5 \times 10^5$, $[CuL_2]/[CuL][L] = 1.8 \times 10^2$, $[CuL_3]/[CuL_2][L] = 7$. [c] Determined by vpc analysis *vs.* hexadecane as the added internal standard.

Table VIII
Calculated Equilibrium Concentrations *vs.* Benzophenone Yield for Bis(γ-collidine)copper(I) Perchlorate, L_2CuClO_4[a,b]

Concn, *M*						Yield of benzophenone
Total ligand × 10^2	Total metal × 10^2	Free ligand × 10^2	Free metal × 10^9	LCu × 10^4	L_2Cu × 10^2	(**2**), %[d]
6.00	3.00	0.212	114	21.2	2.79	10.3
7.00	3.00	1.04	5.01	4.56	2.95	12.8
12.7	3.00	6.71	0.123	0.720	2.99	27.7
14.7	3.00	8.71	0.0733	0.5555	3.00	31.5
16.7	3.00	10.7	0.0485	0.452	3.00	30.8
23.7	3.00	17.7	0.0177	0.273	3.00	25.3

[a] Reference 12. [b] Equilibrium constants used were[c] $[CuL]/[Cu][L] = 8.7 \times 10^6$, $[CuL_2]/[CuL][L] = 6.2 \times 10^3$. [c] Approximated using the relationships $\log K_1 = a\mathrm{p}K_a + b$ and $(K_1/K_2)_{\gamma\text{-collidine}} = (K_1/K_2)_{2\text{-picoline}}$. [d] Determined by vpc analysis *vs.* hexadecane as the added internal standard.

Table IX
Calculated Equilibrium Coxcentrations *vs.* Benzophenone Yield for Bis(2,6-lutidine)copper(I) Perchlorate, L_2CuClO_4[a,b]

Concn, *M*						Yield of benzophenone
Total ligand × 10^3	Total metal × 10^2	Free ligand × 10^2	Free metal × 10^9	LCu × 10^4	L_2Cu × 10^2	(**2**), %[d]
6.00	3.00	0.587	1000	58.7	2.41	4.1
7.70	3.00	1.91	109	20.9	2.79	9.0
9.40	3.00	3.52	33.3	11.7	2.88	11.3
12.8	3.00	6.86	8.92	6.12	2.94	15.0
17.7	3.00	11.7	3.07	3.61	2.96	22.5
26.4	3.00	20.4	1.02	2.08	2.98	23.4
36.0	3.00	30.0	0.474	1.42	2.99	28.6
43.0	3.00	37.0	0.312	1.15	2.99	18.2

[a] Reference 12. [b] Equilibrium constants used were[c] $[CuL]/[Cu][L] = 1 \times 10^6$, $[CuL_2]/[CuL][L] = 7 \times 10^2$. [c] Approximated using the relationships $\log K = a\mathrm{p}K_a + b$ and $(K_1/K_2)_{2,6\text{-lutidine}} = (K_1/K_2)_{2\text{-picoline}}$. [d] Determined by vpc analysis *vs.* hexadecane as the added internal standard.

If $b = 1.32$ (as is k_H/k_D foPh· + PhOH → PhH + PhO·), then

$$7.3a = 22.7 - (5.3 \times 1.32) = 22.7 - 6 = 16.7$$

$$a = \frac{16.7}{7.3} = 2.3$$

If $a = 1$ (as is k_H/k_D in free-radical arylation) then

$$5.3b = 22.7 - 7.3 = 15.4$$

$$b = \frac{15.4}{5.3} \cong 3$$

Calculated Equilibrium Concentrations *vs.* Benzophenone Yield. See Tables VI–IX.

Registry No.—**1**, 342-62-1; **2**, 119-61-9; **3**, 117-99-7; **4**, 486-25-9; **5**, 24018-00-6.

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Formation of Nitrate Esters in Thallium(III) Nitrate Oxidation of Alkenes[1]

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Received March 5, 1974

The oxidation of alkenes with $Tl(NO_3)_3 \cdot 3H_2O$ (TTN) in methanol is known to lead to the formation of dimethoxy and carbonyl compounds. However, examination of the oxidation of 1-decene, 2,3-dimethyl-2-butene, and *cis*- and *trans*-stilbene indicates that methoxy nitrates and dinitrates are also formed. A net trans addition is observed in the formation of dimethoxy, methoxy nitrate, and dinitrate products from *cis*- and *trans*-stilbene.

In the course of a kinetic study[2] of the reaction of alkenes with thallium(III) nitrate (TTN) in methanol it became desirable to investigate the products formed. The oxidation of aliphatic alkenes with TTN has been reported to lead to the formation of ketones and glycol dimethyl ethers.[3] The reaction of cyclic alkenes with TTN leads to the formation of ring-contracted carbonyl compounds.[4] The formation of glycol mononitrate esters (5–15%) believed to arise from a minor side reaction was reported in a footnote[5] by Taylor and McKillop in the latter study.[4] However, no further details of the identity of the products were given. As a result of our study we now report that the formation of nitrate esters from the reaction of TTN with alkenes may be a more general process than previously suspected.

Results

The reaction of 1-decene (I), 2,3-dimethyl-2-butene (VI), and *trans*- and *cis*-stilbene (XI and XVI) with TTN in methanol was investigated in detail. Other alkenes such as *cis*-3-hexene, cyclohexene, and 1-buten-3-ol also yield nitrate esters as verified by the presence of ir bands at 1640, 1280, and 870–840 cm^{-1}. These alkenes were not as amenable to product analysis as the four compounds chosen. Each mixture of products was isolated, dissolved in carbon tetrachloride, and examined by pmr. The products were identified by comparison with the pmr of authentic samples prepared by independent methods. Where possible an individual component was isolated and compared spectroscopically with an authentic sample. The yield of each component in the mixture was determined from the area of readily identifiable resonances in the pmr. Attempted analysis of the product mixture by gc on a number of columns was unsuccessful. The instability of nitrate esters on the columns at the temperatures employed precluded this analytical method.

1-Decene (I). Reaction of I in methanol with TTN at 0° leads to the formation of 1,2-dimethoxydecane (II, 33–42%), 2-decanone (III, 34–40%), and 2-methoxy-1-decyl nitrate (IV, 23–27%).

$$\underset{\mathrm{I}}{C_8H_{17}CH{=}CH_2} \xrightarrow[CH_3OH,\,0^\circ]{TTN} \underset{\mathrm{II}}{C_8H_{17}CH(OCH_3)CH_2(OCH_3)} + \underset{\mathrm{III}}{C_8H_{17}COCH_3} + \underset{\mathrm{IV}}{C_8H_{17}CH(OCH_3)CH_2(ONO_2)}$$

Two methoxy singlets at δ 3.26 and 3.30 establish the presence of II in the reaction mixture. An authentic sample of II was prepared by the acid opening of 1,2-epoxydecane in methanol, followed by reaction of the resultant mixture of methoxy alcohols with diazomethane. The pmr of III has been previously reported[6] and is distinguished by a methyl singlet at δ 2.04. Authentic IV was obtained by the nitration of 2-methoxy-1-decanol. Although the protons on the carbon bearing the nitrate group in IV are the AB portion of an ABX spin system, they appear as a doublet at δ 4.35. 2-Methoxy-1-decyl nitrate was isolated from the reaction mixture by eluting the products through a silica gel column (100–200 mesh, 300 × 20 mm) with 400 ml of pentane fol-