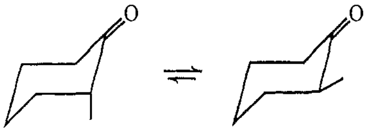
that if complexation of the carbonyl group by hydride is a step in the reduction of cyclohexanones by lithium tri-*tert*-butoxyaluminohydride, it is not rate determining. However, they further pointed out that this does not mean that such complexation is not important in determining stereochemistry. We wish to report for the first time stereochemical results that demonstrate that complexation of the carbonyl group by a metal cation does occur in reduction of ketones by complex metal hydrides and that the stereochemical outcome is affected by such complexation.

The increase of apparent equatorial attack on 2-methylcyclohexanone (I) over that observed with 4-*tert*-butylcyclohexanone (II) by $LiAlH_4$ and other reducing agents has been explained by (1) an increase in the steric requirement for axial attack on Ie and (2) axial attack on conformer Ia which produces the same alcohol (cis) as if equatorial attack had taken place on Ie.[5]



Ia Ie

Table I shows the extent of apparent equatorial attack on I and II by $LiAlH_4$, $ClMgAlH_4$, and $Mg(AlH_4)_2$. The trend shows an increase in equatorial attack on Ie which is rather surprising since the same hydrides show little variation in their reaction with II. This decrease in axial attack on Ie cannot be explained by an increase in steric hindrance toward axial attack since $ClMgAlH_4$ and $Mg(AlH_4)_2$ give more exo attack on camphor and more axial attack on 3,3,5-trimethylcyclohexanone[6] than $LiAlH_4$.

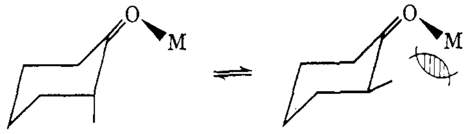
If steric hindrance is the governing factor, then reduction of *cis*-2-methyl-4-*tert*-butylcyclohexanone (III) by the same hydrides should result in decreased axial attack as the steric requirement of the hydride increases. The results of our study show the steric requirement of each hydride to be nearly the same. We conclude from these results that more of conformation Ia is involved in the reduction of I by $Mg(AlH_4)_2$ and $ClMgAlH_4$ than by $LiAlH_4$.

Table I. Cis Alcohol from the Reaction of Complex Metal Hydrides with Cyclohexanones

Hydride[a]	I[c]	II[c]	III[d]
$LiAlH_4$[b]	24	10	17
$LiAlH_4$	25	8	17
$ClMgAlH_4$[b]	36	10	21
$ClMgAlH_4$	43	10	21
$Mg(AlH_4)_2$[b]	49	13	27
$Mg(AlH_4)_2$	49	14	27

[a] THF, 0°. [b] Excess hydride. [c] Purified commercial samples. [d] Pure synthetic sample.

It has been shown that lithium and magnesium salts or protic solvents[7] catalyze borohydride reduction of ketones and esters. A mechanism suggested[1] for ketone reduction by $LiAlH_4$ involves prior or concurrent association of the carbonyl oxygen with Li^+ as the hydride is transferred. Such a mechanism is supported by the results reported here. If complexation of the carbonyl group occurs during reduction, then the concentration of IaC (and its transition state corresponding to axial attack) should increase relative to Ia because the equatorial methyl group sterically interacts with the complexing agent and the energy difference between IaC and IeC is less than that between Ia and Ie. Therefore, since there is no reason to expect a slower rate of axial attack on IaC than IeC, it is not surprising that more reaction proceeds through IaC (Ia) with bulkier complexing agents, $-MgCl^+$ and $-MgAlH_4^+$, than with a smaller complexing agent, Li^+.



IaC IeC

In the case of III the methyl group is fixed in an equatorial position, and, because a change in conformation cannot easily occur, the stereochemical outcome is nearly the same with all three hydrides. The results do not vary as with I where the conformation of the 2-methyl group can change from equatorial to axial positions.

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E. C. Ashby,* J. R. Boone, J. P. Oliver
School of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

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Thermolysis of Aryloxypyridinium Salts. Possible Generation of Aryloxenium Ions

Sir:

There has been much activity recently in connection with the intermediacy of phenoxenium[1] ions (the names phenoxonium and phenoxylium have also been used), particularly in biosynthetic-type oxidative coupling reactions.[2] In view of this and of our interest in the isoelectronic nitrene and carbene reactive intermediates, we have sought an unambiguous method of generating such species and of observing their reactions. Since, by analogy with phenylnitrene, it was expected[3a] that the phenoxenium ion PhO^+ itself might not be electrophilic enough to attack an aromatic nucleus, it was

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[1] The oxenium ion nomenclature is in accord with current usage with the isoelectronic species: nitrenium and carbenium ions.

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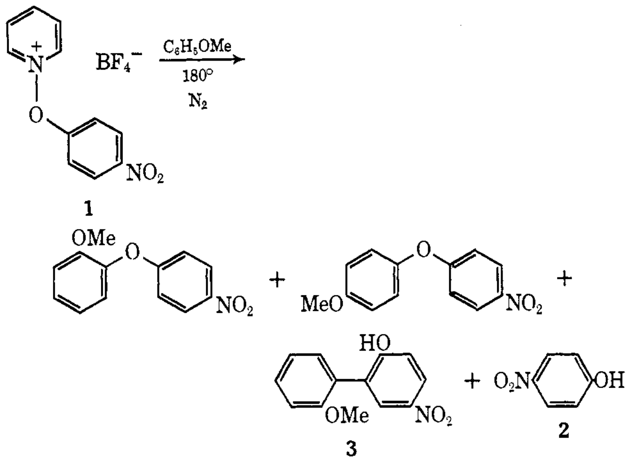
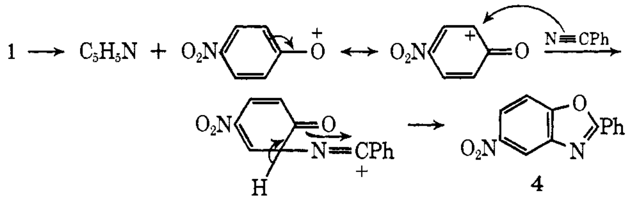
decided to introduce electron withdrawing substituents into the aryl residue. We now report the thermolysis of aryloxypyridinium tetrafluoroborates[3b] in aromatic solvents which suggests that these salts may be sources of $\mathrm{ArO^+}$.



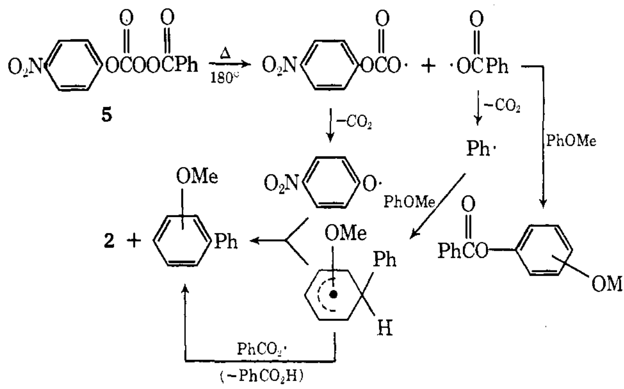
Decomposition of *p*-nitrophenoxypyridinium tetrafluoroborate (**1**) in anisole (degassed) for 5 hr at 180° under N_2 gave a mixture of 2- (24%) and 4-methoxyphenyl 4-nitrophenyl ether (20%), 2-hydroxy-2′-methoxy-5-nitrobiphenyl (**3**) (12%), and *p*-nitrophenol (35%) (**2**). Thermolysis of **1** in mesitylene gave 2,4,6-trimethylphenyl 4-nitrophenyl ether (20%), pyridinium tetrafluoroborate, and **2** (21%) (but no bimesitylyl could be detected), while in *s*-trimethoxybenzene it gave 2,4,6-trimethoxyphenyl 4-nitrophenyl ether (47.6%). Similar products are obtained from the corresponding *o*-nitro- and *o*-trifluoromethylphenoxypyridinium salts and anisole and from **1** and phenol, but the product mixtures have not been completely analyzed yet. To our knowledge these represent the first examples of intermolecular aromatic aryloxylation.

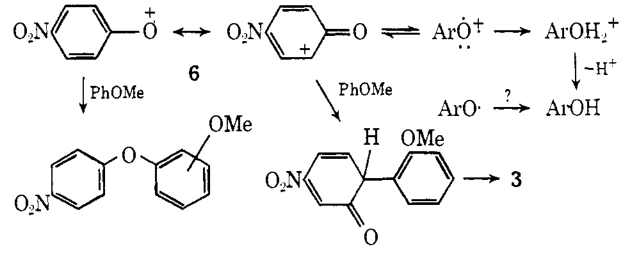
Three possible mechanisms can be envisioned to account for the products formed. (i) Homolytic N–O bond fission to give ArO· and $\mathrm{C_5H_5N\cdot^+}$. Such a process has been reported by Mee, Heseltine, and Taylor[4] in the photodecomposition of *N*-methoxyphenanthridinium perchlorate which was said to give methoxyl radicals. ArO· would then add to Ar′H to form a σ complex from which ArOAr′ and ArOH would result by H abstraction. (ii) Heterolytic N–O cleavage to give pyridine and $\mathrm{ArO^+}$. The latter, by analogy with carbenes and nitrenes, could exist either as a singlet ($\mathrm{Ar\ddot{O}^+}$) or a triplet ($\mathrm{Ar\dot{O}\cdot^+}$). The former would attack Ar′H as do other electrophilic reagents, while the latter (probably the ground state) would abstract hydrogen to give $\mathrm{ArOH_2^+} \rightarrow \mathrm{ArOH} + \mathrm{H^+}$. (Phenol formation could also arise by a competing process leading to ArO· which then abstracts hydrogen). (iii) A concerted nucleophilic attack by anisole upon the developing positive charge simultaneous with the departure of the pyridine, so that a "free" aryloxenium ion is not formed.

In order to distinguish between i and ii the decomposition of **1** in degassed benzonitrile at 180° was studied. The main products were 5-nitro-2-phenylbenzoxazole (**4**) (35%) and **2** (28%); no attack apparently took place on the benzene ring of the benzonitrile, in contrast to the results obtained[4] from the photolysis of *N*-methoxyphenanthridinium perchlorate in this solvent. This is best accounted for by mechanism ii, though iii cannot be ruled out



Since little is known about the intermolecular reactions of unhindered aryloxy radicals in nonprotic media, an attempt was made to oxidize *p*-nitrophenol in anisole with $\mathrm{Ag_2CO_3}$ on Celite,[5] but only starting phenol was recovered. Similarly, reaction of thallium trifluoroacetate[2g] with **2** in anisole led, as expected, to extensive reaction of the reagent with the anisole, but not with **2**. *p*-Nitrophenoxy radical was generated by the thermolysis of perbenzoyl *p*-nitrophenyl carbonate (**5**), mp 92–93° (per cent peroxide 99.12%).[6] When **5** was heated in anisole at 180°, **2** (60%), benzoic acid (20%), and *o*- and *p*-anisyl benzoates were formed, together with the three possible methoxybiphenyls.[7] No nitrodiphenyl ethers or nitrobiphenyls were formed, indicating that a different reactive intermediate was formed from **1** and that nitrophenoxy radicals do not effect homolytic aromatic substitution. Similarly, thermolysis of **5** in benzonitrile gave **2** (62%) but *no* **4**.[7] These facts, together with the absence of bimesitylyl from the thermolysis of **1** in mesitylene, rule out the participation of an aryloxy radical as the key intermediate in the decomposition of **1**. The diphenyl ether and nitrobiphenyl formation from **1** in anisole are best accounted for by invoking attack of the activated aromatic nucleus by a *p*-nitrophenoxenium ion (**6**).





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(6) All new compounds were fully characterized by their spectral and analytical properties and by comparison with authentic samples in most cases. Yields reported are isolated yields.

(7) Oligomeric or polymeric material was also formed.

The greater proportion of C–O over C–C bond formation also speaks[2e] in favor of the cationic mechanism.

In the absence of kinetic data it is not possible to rule out a concerted process (iii). If it obtains, however, N–O bond cleavage will have to have proceeded to a very large extent to account for the formation of compounds such as **3** and **4** (from rather poor nucleophiles).

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R. A. Abramovitch,* M. Inbasekaran, S. Kato
Department of Chemistry, University of Alabama
University, Alabama 35486

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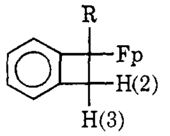
A Novel Cationic Carbene Complex Lacking Heteroatom Stabilization

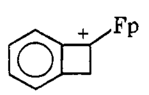
Sir:

Although numerous carbene complexes[1] are known, the carbene ligand almost without exception must possess some special form of stabilization. Thus, the ligating carbon is most commonly (1) bonded to an adjacent heteroatom possessing nonbonding pairs of electrons, (2) incorporated into an aromatic nucleus, or (3) bonded to a cluster of metal atoms. In the absence of stabilizing groups or structures, carbene complexes are apparently too reactive to be isolated. Complexes containing unstabilized carbene ligands have been proposed as intermediates during the reactions of chloromethyl[2] and cyclopropyl complexes[3] and the transition metal catalyzed rearrangement of strained hydrocarbons.[4] We now report the serendipitous preparation and isolation of h^1-1-benzocyclobutenylidene-h^5-cyclopentadienyldicarbonyliron hexafluorophosphate (**2**)—a carbene complex lacking special stabilization.

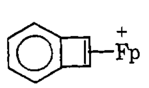
We are interested in *dihapto*cyclobutadienoid transition metal complexes and set out to generate such a complex of benzocyclobutadiene (**3**) by β-hydride abstraction from h^1-1-benzocyclobutenyl-h^5-cyclopentadienyldicarbonyliron (**1a**), which was prepared in 50% yield by the addition of sodium h^5-cyclopentadienyldicarbonylferrate to 1-bromobenzocyclobutene:[5] **1a**; ir (neat) 2003, 1942 cm^{-1} (C≡O); nmr (CS_2) τ 5.95 (m, 1, ^{1}H), 7.31 (m, 1, $J_{^1H^2H}$ = 2.1 Hz, $J_{^2H^3H}$ = 13.5 Hz, ^{2}H), 6.56 (m, 1, $J_{^1H^3H}$ = 4.9 Hz, ^{3}H), 5.37 (s, 5, Cp), 3.18 (m, 4, Ar). Surprisingly, treatment of **1a** with trityl hexafluorophosphate in methylene chloride gave **2** in yields up to 90% as deep orange-red crystals.[6] The spectroscopic properties of **2** alone are not sufficient to distinguish between structures **2** and **3**. Thus, the nmr (CD_3NO_2) spectrum of **2** exhibited singlets at τ 5.35 and 4.10 and a multiplet centered at 2.17 with relative intensities of 2:5:4. The aromatic multiplet was, however, not of the AA′-BB′ type and therefore appeared to be inconsistent with **3** which normally would be expected to possess a plane of symmetry. The carbonyl stretching frequencies of **2** (2065 and 2020 cm^{-1}) are very similar to those observed for the cationic olefin complexes of h^5-cyclopentadienyldicarbonyliron. A clear distinction between structures **2** and **3** is possible on the basis of the chemistry of **2**. **2** is readily reduced by lithium aluminum hydride in diethyl ether to **1a**. The use of the analogous deuteride gave **1b**, the nmr spectrum of which exhibited two doublets at τ 6.53 and 7.28 with $J_{^2H^3H}$ = 14.7 Hz in addition to the resonances attributed to the aromatic and cyclopentadienyl protons. The large coupling constant clearly indicates that the protons on the four-membered ring are geminal[7] and that the deuterium is attached to the ligating carbon. Treatment of **1b** with trityl hexafluorophosphate results in the formation of **2** without incorporation of deuterium and thereby demonstrates that **2** is formed by direct α-hydride abstraction.



1a, R = H(1)
b, R = D
c, R = OMe
d, R = OH
e, R = PPh$_3$$^+$



2



3

Fp = h^5-CpFe(CO)$_2$

Although **2** is stable when cold and under nitrogen, it slowly decomposes in moist air at room temperature. **2** rapidly decomposes in the presence of nucleophilic solvents such as tetrahydrofuran, acetone, alcohols, or water but is indefinitely stable in degassed anhydrous nitromethane, sulfur dioxide, or methylene chloride. As might be expected **2** behaves in a manner similar to the trityl salts and forms a number of 1:1 adducts with a variety of nucleophiles. The methoxy adduct (**1c**) is readily prepared by dissolving **2** in methanol in the presence of sodium bicarbonate: **1c** ir (Nujol) 1989, 1916 cm^{-1} (C≡O); nmr (CS_2) τ 6.76 (s, 3, CH_3), 6.78 (d, 1, J = 13.5 Hz, ^{2}H) 6.43 (d, 1, ^{3}H), 5.25 (s, 5, Cp), 3.01 (m, 4, Ar). The hydroxy adduct (**1d**) prepared by treatment of a methylene chloride solution of **2** with aqueous sodium bicarbonate is unstable and readily decomposes to benzocyclobutenone and h^5-cyclopentadienyldicarbonyliron dimer. Triphenylphosphine also adds to **2** to form the adduct **1e**. Treatment of **2** with lithium iodide in anhydrous nitromethane resulted in the formation of 1-iodobenzocyclobutene, h^5-cyclopentadienyldicarbonyliron iodide, and **1a**. **2** is also a potent hydride abstractor, capable of converting cycloheptatriene to the tropylium ion and ethyl-h^5-cyclopentadienyldicarbonyliron to the cationic ethylene complex. Attempts to alkylate or deprotonate **2** with organomagnesium or -lithium reagents or tertiary amines

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