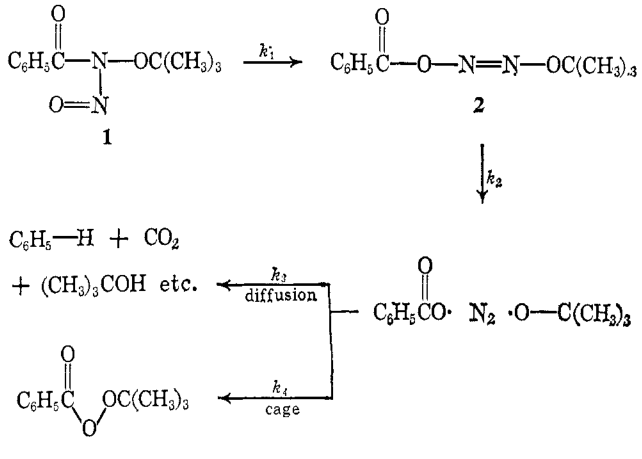
We are presently testing the above conclusions using oxygen-18 labeling techniques and hope to establish a scale of acyloxy radical stabilities with compounds analogous to **1**. We also are comparing reactivities of the acyloxy radical intermediates generated in this way with those generated from perester decompositions.



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Complete Stereochemical Rearrangement in a Cobalt(III) Reaction in Acidic Solution

Sir:

During investigations of intermediate-field cobalt(III) isomers, we have noted a surprisingly stereospecific reaction which appears to be the first example of complete stereochemical change for a cobalt(III) substitution reaction in acidic media. Recent stereochemical results on triethylenetetramine complexes of cobalt(III) also show unexpected results when compared with the corresponding ethylenediamine complexes,[1] but the triethylenetetramine rearrangement involves base hydrolysis, which often results in considerable configurational change.[2]

Both the blue *cis* and the violet *trans* isomers of the $[Co^{III}(CO_3)_2(NH_3)_2]^-$ anion[3] yield only the *cis*-$[Co(acac)_2(NH_3)_2]^+$ isomer when two acetylacetonato (acac) ligands replace two carbonato groups. Reaction conditions were such that *trans* → *cis* isomerization of the product would be negligible.

In each case, the dicarbonato complex (1 mole) was dissolved in water immediately after its preparation by a slight modification of the original synthetic method,[3] and treated with 2,4-pentanedione (2 moles) and then 6 *M* acetic acid, which was added dropwise to a pH of about 6 or until completion of carbon dioxide evolution. (Dilute HCl has also been substituted in the preceding step satisfactorily.) Rapid fractional crystallization *in vacuo* at room temperature using rotary evaporation gave no indication of any *trans*-$[Co(acac)_2(NH_3)_2]^+$. Small amounts of $[Co(acac)_3]$, necessarily of a *cis*-type orientation, were also formed and extracted with chloroform. These identical results were obtained for numerous runs with each isomer and were substantiated by microscopic examination, proton magnetic resonance, and infrared and visible spectroscopy. All of the properties of the products are identical with those reported for the *cis* isomer.[4]

Proof that the single isomer is not due to isomerization is based on the previous preparation of the pure *cis* and *trans* isomers of $[Co(acac)_2(NH_3)_2]^+$ by a tedious fractional crystallization procedure which involved similar environmental conditions.[4] That is, the *cis* and *trans* isomers did not isomerize during the recrystallizations which involved up to several days in aqueous solution and pH and temperature conditions similar to those of the present investigation.

These results substantiate the contention of Basolo and co-workers[5] that complex ion electronic effects have been overemphasized and that more attention should be paid to steric factors. Furthermore, Chan and Tobe[6] have suggested that the aquation results of bis(ethylenediamine)-type cobalt(III) complexes can best be correlated by considering the activation process as involving a movement of the five retained coordinated species toward a trigonal bipyramidal structure, even in substitution reactions which give complete retention of configuration. If this were true, protonation of bis(carbonato) species would lead to an intermediate similar to that shown as intermediate I. The alternate intermediate in which both ends of the carbonate group are in the trigonal plane requires enlarging the O–Co–O angle of the four-membered ring beyond 90°, which is unlikely since the normally tetrahedral Co–O–C bond angles are already somewhat strained in the parent complex. The opposite effect is expected in the subsequent step since the six-membered acetylacetonato chelate ring is expected to be less strained at an angle of $>90°$ than at the 90° angle of the octahedral complex. Hence, the intermediate II is favored for the second replacement. Aquo intermediates may be involved. Even so, it would appear that loss of the first carbonato species would be the most likely step for the stereospecific reaction.

These results also explain the predominant retention of configuration observed in the reaction of tricarbonatocobaltate(III) with 2 moles of ammonia[3] since the expected intermediate would be similar to structure III. On the other hand, the blue *cis*-dicarbonato salt has also been reported to produce *trans*-$[Co^{III}(NO_2)_4(NH_3)_2]^-$ in about 75% yield,[7] with evidence for the *trans* structure based on the similarity of the ultraviolet spectrum with that of the *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ ion

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[1] E. Kyuno, L. J. Boucher, and J. C. Bailar, *J. Am. Chem. Soc.*, **87**, 4458 (1965); E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1120, 1125 (1966).

[2] For a recent review see C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 3.

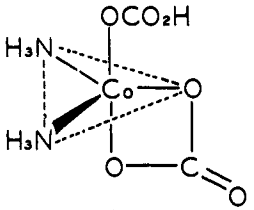
[3] M. Mori, M. Shibata, E. Kyuno, and T. Adachi, *Bull. Chem. Soc. Japan*, 29, 883 (1956).

[4] R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

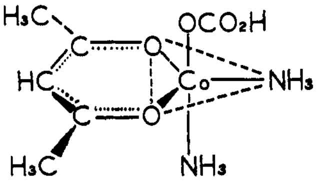
[5] W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2944 (1966); C. F. Weick and F. Basolo, *Inorg. Chem.*, **5**, 576 (1966); W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

[6] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

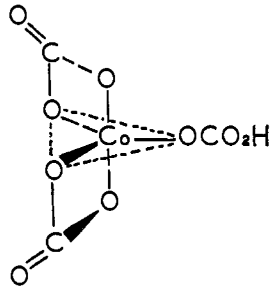
[7] M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).



I



II



III

as prepared by other means, for which the structure is known.[8] Since the *trans*-tetranitrodiamminecobaltate(III) salt precipitated from solution after standing, isomerization of an original soluble *cis* intermediate would account for the results in that synthesis. Further work is in progress to substantiate the implied mechanism, to determine the possible role of aquo intermediates, and to compare the product composition for varied ring size.

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(8) Y. Komiyama, *Bull. Chem. Soc. Japan*, 29, 300 (1956); Y. Komiyama, *ibid.*, 30, 13 (1957).

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The Production of Organocopper Intermediates from Radicals in the Reactions of Aromatic Halides and Diazonium Ions with Cuprous Benzoate. New Synthetic Methods for Aryl Benzoates[1]

Sir:

We have recently presented evidence[2a] that the copper metal induced coupling of *p*-iodotoluene in quinoline proceeds *via* an organocopper intermediate[2b] which, in addition to being capable of self-coupling (reaction G), can be captured by acids (F) to produce toluene.[3] In the present communication it is shown that organocopper intermediates, exhibiting similar behavior, can also be prepared by the reaction of cuprous benzoate with aromatic halides or diazonium ions, and some new reactions of these intermediates are disclosed.

It has been reported[4] that cuprous acetate and benzoate execute a reductive dehalogenation on aryl halides in nitrogen heterocyclic solvents. In our hands, a good yield of aryl benzoate, along with some arene (reduction product), was obtained from the reaction of an aryl halide and cuprous benzoate; however, rigorously anhydrous conditions were necessary for such suppression of the reduction reaction. Although pyridine can be used as the medium, better yields are obtained in diglyme or xylene. Thus, aryl benzoates are obtained in the specified yields when the following aryl halides are treated at 140–160° with cuprous benzoate:[5] *p*-iodotoluene (94%), *p*-bromotoluene (79%), α-bromonaphthalene (51%), *p*-bromoanisole (85%), *m*-nitrobromobenzene (62%), and *p*-nitrobromobenzene (34%; a fairly large but undetermined amount of *p*-nitrophenol was produced in workup). A mixture of *cis*- and *trans*-2-bromo-2-butene gives a mixture of enol benzoates by the same procedure. *This appears to be the only general method for the direct preparation of phenol and enol benzoates from aryl and vinyl halides.*

In several of the aryl cases, coupling products (biaryls) accompany the esters.[6] Furthermore, the addition of benzoic acid to the reaction medium drastically decreases the yield of substitution product and leads to the formation of arene (Ar–H). This behavior strongly suggests the intermediacy of an organocopper capturable by protonation (F);[2a] in the absence of proton sources, the intermediate undergoes conversion (C) to aryl benzoate and/or to biaryl [*via* self-coupling (G) or reaction with aryl halide (H)[2]].

On the basis of recent reports,[8] the reaction of a cuprous salt with an aryl halide most likely produces (A) an aryl radical.[9] This radical must react (B) extremely rapidly with cuprous benzoate to produce an organometallic[3] since very little if any reaction of the radical with the solvent occurs.

$$\mathrm{ArX} + \mathrm{CuOBz} \longrightarrow \mathrm{Ar}\cdot + \mathrm{XCuOBz} \qquad \text{(A)}$$

$$\mathrm{Ar}\cdot + \mathrm{CuOBz} \rightleftharpoons \mathrm{ArCuOBz} \qquad \text{(B)}$$

Independent evidence for the key steps A and B has been obtained. (A) We resorted to a very sensitive intramolecular trap to demonstrate the formation of an aryl radical. The production of N-methylbenzamide (**2**) from the reaction of *o*-bromo-N,N-dimethylbenzamide (**1**) with cuprous benzoate is strongly indicative that an intermediate aryl radical has been trapped by a

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(1) This work was supported by Grant GP 3821 from the National Science Foundation.

(2) (a) A. H. Lewin and T. Cohen, *Tetrahedron Letters*, **No. 50**, 4531 (1965); (b) M. Nilsson, *ibid.*, **No. 7**, 679 (1966).

(3) The exact nature of the organometallic has not yet been determined. However, phenylcopper, involving Cu(I), is known to undergo self-coupling with the deposition of a copper mirror: R. Reich, *Compt. Rend.*, **177**, 322 (1923); H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891 (1966).

(4) R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.* (London), **19**, 95 (1965).

(5) The salt was preformed (i) by heating equivalent quantities of cuprous oxide and benzoic acid in xylene with continuous removal of the water by azeotropic distillation or (ii) by heating cuprous oxide with benzoic anhydride in diglyme at 160° for 10 hr.

(6) Numerous examples of such couplings occurring during the reactions of aryl halides with cuprous salts have been noted.[4,7]

(7) L. J. Belf, M. W. Buxton, and G. Fuller, *J. Chem. Soc.*, 3372 (1965); R. G. R. Bacon and O. J. Stewart, *ibid.*, 4954 (1965).

(8) M. Asscher and D. Vofsi, *ibid.*, 4962 (1964); M. Asscher and D. Vofsi, *ibid.*, 1887, 3921 (1963).

(9) The reverse process is a well-established reaction type.[10]

(10) (a) A. H. Lewin, A. H. Dinwoodie, and T. Cohen, *Tetrahedron*, **22**, 1527 (1966); (b) J. K. Kochi, *ibid.*, **18**, 483 (1962); (c) J. K. Kochi and H. E. Mains, *J. Org. Chem.*, 30, 1862 (1965); (d) A. H. Lewin and T. Cohen, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract K103.