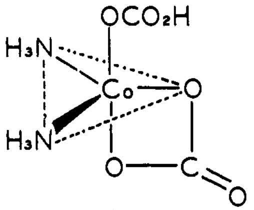

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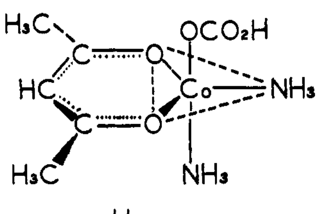

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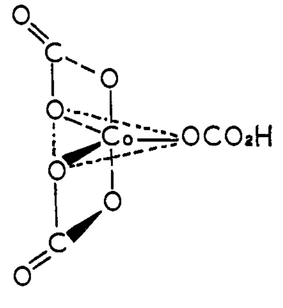

III

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).

(9) Address correspondence to the Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002. Support of the National Science Foundation through GP-2938 is gratefully acknowledged.

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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 work-up). 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.

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

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

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.

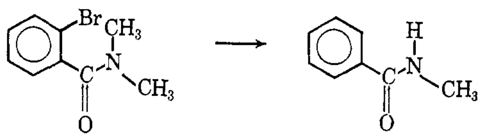
(6) Numerous examples of such couplings occurring during the reactions of aryl halides with cuprous salts have been noted.[4,7]

(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]

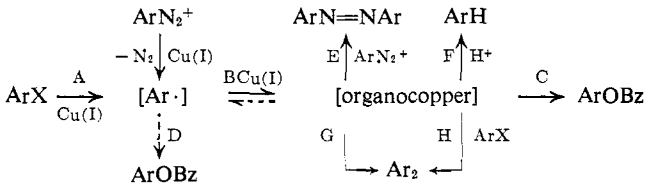
(10) (a) A. H. Lewin, A. H. Dinwoodie, and T. Cohen, *Tetrahedron*, **22**, 1527 (1966); (b) J. K. Kochi, *ibid.*, **18**, 483 (1962); (c) J. K. Kochi and H. E. Mains, *J. Org. Chem.*, 30, 1862 (1965); (d) A. H. Lewin and T. Cohen, 151st National Meeting of the American Chemical Society, Pittsburgh,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



1 2

1,5-hydrogen atom transfer.[10a] (B) Evidence to support the novel concept that aryl radicals can react readily with cuprous benzoate to form organometallics was obtained by treating *p*-toluenediazonium fluoroborate dissolved in sulfolane with cuprous benzoate in diglyme. A rapid evolution of nitrogen occurred and the typical arylcopper coupling product, bitolyl,[2a] was produced along with *p*-tolylbenzoate, toluene, and *p,p'*-dimethylazobenzene. It is now well established that radicals are produced upon decomposition of diazonium ions induced by Cu(I).[10a,d,11] Biaryls and azoarenes are frequently observed products from the copper-promoted decomposition of diazonium ions, and their mode of formation has never been satisfactorily explained.[4,12] It now seems likely that they are both formed from organocopper intermediates, coupling[2a,3] (G) of which produces biaryl and addition (E) of which across the nitrogen–nitrogen bond of the diazonium ion leads to azoarene.[13,14a]

The mechanism of the formation (C) of the aryl benzoate from the organometallic intermediate remains obscure. It would be tempting to postulate that organocopper formation from the radical is reversible (see B) and that the aryl radical is capable of abstracting a benzoyloxy radical from a Cu(II) salt of benzoic acid[10a,d] (broken arrows B and D), but we have found that cupric benzoate does not react with phenyl radicals generated by cuprous oxide catalyzed decomposition of the *p*-toluenediazonium ion.[15]



The results reported here and summarized in the above scheme suggest mechanistic explanations for a number of known copper-induced reactions, and this topic will be explored in subsequent papers.

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(11) J. K. Kochi, *J. Am. Chem. Soc.*, **79**, 2942 (1957); S. C. Dickerman and G. B. Vermont, *ibid.*, **84**, 4150 (1962); C. S. Rondestvedt, *Org. Reactions* **11**, 189 (1960).

(12) W. A. Cowdrey and D. S. Davies, *Quart. Rev.* (London), **6**, 358 (1952); E. Pfeil, *Angew. Chem.*, **65**, 155 (1953).

(13) This explanation is in excellent accord with all of the data[4,12] concerning the formation of these by-products of copper-catalyzed diazonium decomposition including the rate dependence on cuprous salt concentration and substituent effects. It should be noted that Grignard and organozinc compounds have been reported to yield azo compounds on treatment with diazonium salts.[14]

(14) H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 274 (1945); D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.*, **21**, 1221 (1956).

(14a) NOTE ADDED IN PROOF. It has been called to our attention that a similar suggestion has been tentatively put forth by Kochi (footnote 19 of ref 11).

(15) However, the cupric benzoate was only slightly soluble in the diglyme–sulfolane reaction medium. Furthermore, a very specific form of the Cu(II) salt might be required.[10c]

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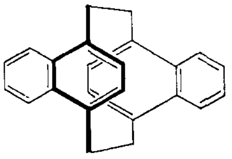
The Photosensitized Autoxidation of [2.2]Paracyclonaphthane

Sir:

While aromatic systems such as anthracene and rubrene readily form transannular peroxides with air and light,[1,2] such sensitivity toward singlet oxygen has not been exhibited by naphthalene or benzene.[3]

We now wish to report that the strained naphthalene system in anti[2.2]paracyclonaphthane (I)[4] reacts with oxygen under the conditions of photosensitized autoxidation, leading to the novel polycyclic product, II.



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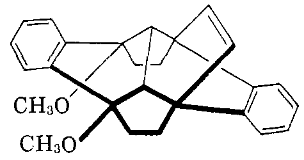

II

Air was passed through a dilute solution of I in methanol in the presence of methylene blue during irradiation with a 275-w G.E. sunlamp.[5] The temperature remained at 58° throughout the reaction, which was stopped after 10 days. On concentrating and cooling the solution, polymeric material and unchanged I was collected. Complete removal of solvent left a residue which, on crystallization from ethyl acetate, yielded the oxidation product (20%) as white needles, mp 209–210°. The assignment of structure II to this product was based on the following evidence: infrared spectrum, peaks at 1080 (C–O) and 2825 cm^{-1} (O–Me); ultraviolet spectrum, λ_{max}^{EtOH} 265 mμ (ϵ 676) (two substituted benzene rings); nmr, multiplet at τ 2.73 (8 aromatic H), singlet at 4.18 (2 vinyl H), singlet at 7.08 (6 methoxyl H),[6] multiplet at 7.63 (10 H). *Anal.* Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07; mol wt, 370. Found: C, 84.57; H, 7.37; mol wt (mass spectroscopy), 370. Thermal breakdown of this product during mass spectral analysis gave rise to peaks at *m/e* 306 and 280, corresponding to loss of two molecules of methanol and an acetylene residue, respectively. On catalytic hydrogenation this product absorbed 1 mole of hydrogen, leading to a dihydro derivative in which the vinyl nmr absorption at τ 4.18 was absent.

The structure which is completely compatible with all of the above physical and chemical data is the internal Diels–Alder addition product II. This conclusion was confirmed by a single-crystal X-ray structure determination carried out by Dr. Albert Fratini of the U. S. Naval Research Laboratories, Washington, D. C.[7]

Formation of II appears to take place by initial reaction of I with singlet oxygen to form a transannular peroxide (III). Although naphthalene normally does not add oxygen in this manner, the strain associated with the ring deformation in the paracyclonaphthane[4] undoubtedly imparts greater reactivity to the dienoid

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(1) C. Dufraisse and J. Houpillart, *Compt. Rend.*, **205**, 740 (1937).

(2) C. Dufraisse and A. Etienne, *ibid.*, **201**, 280 (1935).

(3) C. Dufraisse and R. Priou, *Bull. Soc. Chim. France*, [5] **5**, 611 (1938); C. Dufraisse and J. Houpillart, *ibid.*, [5] **5**, 626 (1938).

(4) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963).

(5) Using visible light (150-w floodlamp) the reaction gave the same product but over a longer period of time.

(6) The abnormally high position of the methoxyl protons may be associated with the shielding effect of the proximate benzene rings.

(7) Details to be reported elsewhere.