

METAL SALT CATALYZED CARBENOIDS: THE ACTIVE FORM OF COPPER IN THE
CATALYZED DECOMPOSITION OF DIMETHYL DIAZOMALONATE

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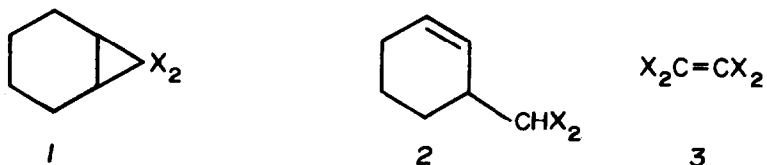
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On occasion, reports have appeared as to the identity of the catalytic species in copper catalyzed decompositions of diazo compounds.¹ Such claims have usually resulted from observations on isolated catalyst after reactions.^{2,3} The inherent weaknesses in such approaches are that changes in valence state result from side reactions, and minor components may exhibit the observed catalytic activity.

We have obtained evidence which indicates that the active species for the decomposition of diazomalonic esters is copper(II). When AR grade copper(0) powder was treated with refluxing cyclohexene (commercial sample, no added peroxide source) for 12 hours, there was no visible change in the hydrocarbon. However, when the reaction filtrate was subsequently treated with dimethyl diazomalonate under standard conditions⁴ in the absence of additional catalyst, we observed a catalyzed reaction (Table I). We feel forced to conclude on the basis of earlier evidence^{1,4-7} that undefined copper(II) species are operative during formal copper(0) catalysis.

While examining in detail the dependence of bis (Methoxy-carbonyl) carbenoid[†] upon catalyst, catalyst concentration, and substrate structure,⁴⁻⁷ we observed that trace amounts of peroxides generate superior catalysts when soluble copper(I) species are employed.⁶ This benefit is realized whether the peroxides are allowed to decompose prior to introduction of diazo compound or during the course of reaction. Thus, if a copper(I) salt is treated with benzoyl peroxide and all peroxide is destroyed, a new active catalyst system results. For a series of parallel reactions, we reported the effect of using: (A) commercial cyclohexene, (B) commercial cyclohexene filtered



Where X = COOCH₃

TABLE I
"Copper (0) Catalyzed" Reactions

Condition *	% Yield		
	1	2	3
Thermal	12.7	Trace	0.00
Cu Metal	38.0	8.05	1.71
Metal free filtrate	36.0	7.20	2.78

TABLE II
The Effect of Peroxide upon the Cu(AcAc)₂ Catalyzed Decomposition
of Dimethyl Diazomalonate in Cyclohexene

Condition *	% Yield		
	1	2	3
Peroxide free	78.5	12.4	5.92
Peroxide present	78.1	12.4	5.81

* All reactions were initiated under nitrogen to prevent atmospheric oxidation.

through alumina, and (C) alumina treated cyclohexene to which 0.07 mmole of benzoyl peroxide was added.⁶

The oxidation of both copper(0)⁹ and copper(I)¹⁰ by radicals is known. During the treatment of copper(I) iodide with benzoyl peroxide, we observed the smooth conversion to copper(II) benzoate and iodine. In the presence of phosphite,⁵ no iodine is observed. At low concentrations of peroxides, it is clear that the anionic ligand associated with the copper catalyst remains attached to copper. This is revealed by the dependence of both yields and product partitioning upon the ionic character of the anion.⁷

The reduction of copper(II) to copper(I) by radicals is also known to occur.¹¹ It therefore seemed prudent to ascertain the effect of the same radicals upon soluble copper(II) catalysts. When copper(II) acetylacetonate was examined in a comparable manner, little change resulted (Table II).

When the trimethylphosphite copper(I) salt complexes are used as formal catalysts, we conclude that undefined copper(II) salts are generated to form the actual catalyst species. Under our conditions this requires the presence of only 0.03% of peroxide impurity in the olefin or 0.14 mmole of some alternate oxidizing agent. Azo-bis-isobutyronitrile is a fair oxidizing agent at comparable levels. Copper(II) fluoroborate was sufficiently soluble to permit its being examined. It proved to be the best catalyst so far encountered in our studies.

Although there is no a priori reason to assume that copper(II) is always the catalyst in diazo decompositions, we feel that existing data on other systems might be worthy of reinvestigation.

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REFERENCES

1. G. W. Cowell, and A. Ledwith, Quart. Rev., 24, 119 (1970).
 2. G. Witting and K. Schwarzenback, Ann. 650, 1 (1961).
 3. M. I. Komendant, I. A. D'yakonov and T. S. Smirnona, J. Org. Chem. USSR (Engl. Transl.), 2, 561 (1966) [C. A., 65, 7124 (1966)].
 4. D. S. Wulfman, B. W. Peace and E. K. Steffen, Chem. Commun., 1360 (1971).
 5. B. W. Peace, F. Carman and D. S. Wulfman, Synthesis, 658 (1971)
 6. B. W. Peace and D. S. Wulfman, Chem. Commun., 1179 (1971).
 7. B. W. Peace and D. S. Wulfman, Tetrahedron Lett, 3799 (1971).
 8. a) G. Santelmann, Dechema - Monographiew, in press.
b) G. Wohllenben, Suppl. to Chimia, 277, 1970.
 9. G. A. Razunaer and V. N. Latyaena, Zhur., 28, 2233 (1958) [C. A., 53, 5186i (1958)].
 10. D. H. Hey, K. S. Y. Liang and M. I. Perkins, Tetrahedron Lett, 1477 (1967).
 11. J. K. Kochi, Science, 155, 415 (1967).
- ‡ We used the term carbenoid to indicate the presence of some type of cabene-catalyst complex as the active species. Supporting evidence for the existence of a carbenoid here, is given in reference 4.