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SOME OBSERVATIONS OF THE EFFICACY OF SOLUBLE COPPER(I) CATALYSTS FOR DECOMPOSING DIAZO COMPOUNDS

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Moser[1] has described studies employing soluble copper(I) catalysts for the decomposition of diazoacetic ester in the presence of olefins and Dave and Warnhoff[2] have given additional details including directions for purification of the catalysts.

There are however several important points of immediate synthetic utility which are not covered in the literature. We have observed the behavior of these catalysts systems with diazomalonic esters[3] which extrapolates to diazoacetic ester and probably to most, if not all, diazo compounds.

Concentration and Precautions: Moser employed relatively large amounts of catalyst, degassed his systems and used perioxide free olefins. These precautions, although desirable for mechanistic studies, are both unnecessary and undesirable for mechanical and chemical reasons during synthetic studies. Thus, the addition of small amounts of radical initiators such as benzoyl peroxide (preferably) or azo-bis-isobutyronitrile (Vazo®[4]) to carefully purified olefins leads to cleaner reactions and higher yields. It also permits using as little as 0.14 mmole of catalyst to decompose 20 mmole of diazo compound whereas Moser had to employ 5.0 mmole. We have determined that the carbenoid process is not radical initiated but rather involves a change of catalyst.[5] Commercial cyclohexene freshly distilled from sodium contains sufficient impurities to promote increased catalyst activity whereas filtration through fresh activated alumina[6] necessitates employing larger quantities of catalyst.

The yields from such reactions are very dependent upon the catalyst concentration, Chart 1 being typical. This is also true of diazoacetic ester (Table 1). A wide range of isomer ratios is obtained by adjusting catalyst concentrations.[7]

Purification of Catalysts: The purification of the catalysts is occasionally desirable. However, if halogenated solvents are employed in recrystallization either singly or with

TABLE 1

PRODUCT DISTRIBUTION FROM THE REACTION OF CYCLOHEXENE, DIAZOACETIC ESTER CATALYZED BY COPPER(I)IODIDE·N×P(OCH$_3$)$_3$ AS A FUNCTION OF N AND CATALYST CONCENTRATION AT 83°

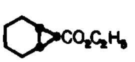
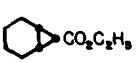
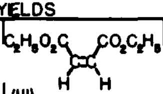
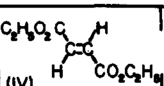
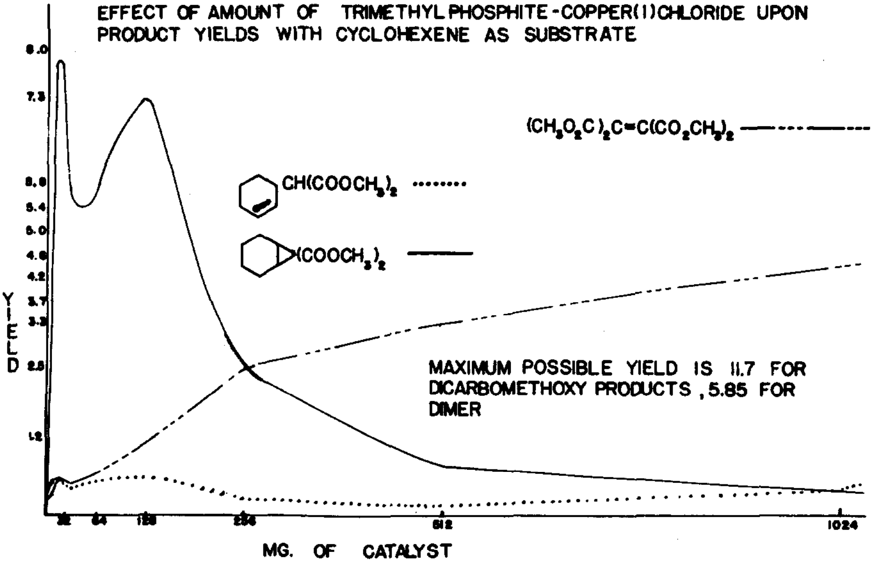
	PRODUCTS AND YIELDS									
M.MOLE OF CAT. AND N	 (I) EXO		 (II) ENDO		EXO/ENDO	 (III)		 (IV)		CIS/TRANS
	ABSOLUTE	RELATIVE	ABSOLUTE	RELATIVE	RATIO	ABSOLUTE	RELATIVE	ABSOLUTE	RELATIVE	RATIO
N = 1										
0.14	7.80	1	0.65	0.083	12.0	0.088	0.011	0.123	0.015	0.715
5.0	2.91	1	1.16	0.390	2.51	0.218	0.075	0.710	0.244	0.307
N = 2										
0.14	7.87	1	0.684	0.087	11.5	0.100	0.012	0.150	0.019	0.667
5.0	0.965	1	0.946	0.980	1.02	0.077	0.079	0.254	0.263	0.304
N = 3										
0.14	8.05	1	0.533	0.066	15.1	0.067	0.008	0.111	0.013	0.608
5.0	0.333	1	0.832	2.50	0.400	NONE		NONE		

CHART 1

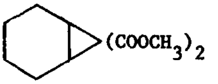
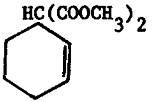


The data in Chart 1 and Tables 1 and 2 was obtained in the following way. A solution of 0.02 mole of diazo compound in 25 ml of cyclohexene (distilled from and stored over sodium) was added to 25 ml of refluxing olefin containing the catalyst. The yields were determined by v.p.c. and are relative to an internal standard. Diazo compounds were carefully distilled to 98.5-99% purity. Traces of chloroacetic ester may interact with the catalysts but clearly different effective catalysts are present in the 3 cases of Table 1.

co-solvents, appreciable destruction of the catalyst can occur. This involves reaction between the phosphite and the halogenated solvent and leads to precipitation of some of the copper(I) salt.[8] Catalysts resulting from this type of treatment contain varying amounts of uncomplexed salt and are less effective than pure material (Table 2).[9]

Table 2

Product Distribution in the Reaction of Cyclohexene with Dimethyl Diazomalonate

	CATALYST 0.14 mmole			$(CH_3OOC)_2C{=}C(COOCH_3)_2$			
		ACTUAL	RELATIVE	ACTUAL	RELATIVE	ACTUAL	RELATIVE
I	$(CH_3O)_3P\cdot CuI$	8.57	1.00	0.930	0.108	0.697	0.081
II	$(CH_3O)_3P\ _3\cdot CuI$	7.67	1.00	1.55	0.202	0.767	0.100
III	$(CH_2O)_3P\ \cdot CuI$	7.40	1.00	0.906	0.122	0.760	0.103
IV	$(CH_3O)_3P\cdot CuCl$	7.45	1.00	1.07	0.144	0.547	0.070
V	IV plus 30 mg CuCl	3.90	1.00	2.70	0.692	0.276	0.071
VI	IV plus 30 mg $CuCl_2$	6.41	1.00	1.45	0.223	0.623	0.097

The phosphite ligand serves as a solubilizing substituent for the copper species but has a deleterious contribution to the overall reaction because of phosphinazine formation.[10] The phosphinazines are readily decomposed under the reaction conditions, both thermally and catalytically.[10] However, the products resulting from the decomposition of the phosphinazine bear no resemblance to the identifiable products of the carbenoid processes.[11]

Table 2 shows the presence of phosphite does have a deleterious effect for diazomalonate and the contribution is not linear. Formal addition of 0.14 mmole increments of phosphite to 0.14 mmole of the mono complex (the bis and tris complexes result) causes a decrease in norcarane yield of approximately 0.9 and an additional 0.3 mmoles. The presence of added copper(I) chloride would be expected to have a slight beneficial effect resulting from reducing the concentration of phosphite because of low solubility. A more deleterious contribution results from the increased common anion. The resultant mixture serves as only a fair catalyst for the desirable processes. The use of copper(II) chloride leads to destruction of the phosphite[12] and any residual copper(II) salt furnishes lesser quantities of anion[13] because the central atom is more highly charged and hence less prone to ionization.[14,15]

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References and Footnotes

1. W. R. Moser, J. Amer. Chem. Soc., 91, 1135, 1141 (1969).

2. V. Dave and E. W. Warnhoff, "Organic Reactions", Vol. 18, Wiley, New York, N.Y., 1970,p 217.

3a. D. S. Wulfman, F. C. Carman, B. G. McGiboney, E. K. Steffen and B. W. Peace, Preprints, Division of Petroleum Chemistry, ACS, 16 (1), B81 (1971) (b) D. S. Wulfman, E. K. Steffen and B. W. Peace, 161st National ACS Meeting, Organic Division, Los Angeles, March 28-April 2, 1971. (c) Further details are to be published elsewhere.

4. Trademark, E. I. du Pont de Nemours & Company.

5. The exact nature of the new catalyst system is currently under investigation. Olefins containing small amounts of peroxides also require much less catalyst although the reactions are not as clean.

6. Alumina filtration has been found to be an efficient means for complete removal of small to moderate quantities of peroxy impurities in hydrocarbons. See Waters Associates Inc., Application Note 105, "Purification of Solvents by Active Alumina."

7. Moser observed an exo-endo ratio range of 6.86 to 5.93 operating in the temperaturerrange 30 to 70°C.

8. The reaction of halocarbons with phosphines is a well recognized reaction both for the formation of phosphonium salts and for halogenation of alcohols to the corresponding halides. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N.Y., 1968, p 1247.

9. The catalyst preparation given in reference 2 was modified. Thus, after removal of the benzene, methanol was added, the mixture cooled and filtered. Catalysts obtained in this way were shown to be pure by m.p., n.m.r. and elemental analysis.

10. For a review of the preparation and decomposition of phosphinazines see A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N.Y., 1966, p 238.

11. D. R. Dalton and S. A. Liebman, Tetrahedron, 25, 3321 (1969), have reported that diphenylmethylene is obtained from the decomposition of a related phosphinazine.

12. We have found the reaction of copper(II) chloride with 2 equivalents of trimethylphosphite in benzene is a convenient means of preparing trimethylphosphite copper(I) chloride.

13. We have found the counter ion when introduced from an alternate source drastically depressed the formation of cyclopropane, insertion product and carbene dimer.

14. Mechanistic details appear in two papers, B. W. Peace and D. S. Wulfman, J. Chem. Soc. (D), (in press).

15. Experimental details appear in B. W. Peace and D. S. Wulfman, Synthesis (in press). We will furnish on request.