The Effect of Peroxides on the Reactions of Dimethoxycarbonylcarbene Generated with Soluble Catalysts from Dimethyl Diazomalonate

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Summary The presence of alkenyl or aryl radicals converts trimethyl phosphite copper(I) iodide into an extremely potent soluble catalyst capable of decomposing diazo-esters cleanly into the corresponding carbenoid species.

For the past several years we have been examining the copper- and copper salt-catalysed decomposition of dimethyl diazomalonate in the presence of some cyclic olefins.[1] The report by Moser[2] that soluble catalysts of the type trialkyl phosphite copper(I) halide are excellent catalysts for decomposing diazoacetic ester led us to extend his studies to dimethyl and di-t-butyl diazomalonates. These studies revealed that under optimum conditions soluble catalysts lead to nearly doubled yields (compared to heterogeneous catalysts), there is a dependence upon catalyst concentration,[3] and that the nature of the counterion influences the overall yields and product distributions.[4] When this is coupled with the effect of added counterion, it becomes clear that the rate-determining step involves displacement of the anionic ligand by diazo-compound.[4]

Although individual batches of olefin behave in a consistent manner, there were large variations in product distributions and yields depending upon which batch of olefin was employed and how it was purified and stored. In addition, we found that we obtained better results than Moser using his system but operating at lower catalyst concentrations. Surprisingly, Moser's catalyst concentration led to very poor results. There was, however, one major difference between the two studies. We did not filter our olefin through alumina† immedately prior to undertaking a reaction as Moser had. When such precautions were undertaken for our system the results were worse than if no catalyst had been employed. We concluded that peroxy impurities in the olefin greatly enhance

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† It has been reported that alumina filtration removes peroxy impurities from hydrocarbons. See Waters Associates Inc., Application Note 105, "Purification of Solvents by Active Alumina."

TABLE

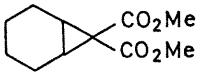
Product distribution and yields in the reaction of cyclohexene and dimethyl diazomalonate as a function of catalyst and peroxide content of the olefin

$(CH_3O)_3P\cdot CuZ$ 0·14 mmole	% Yield			
	(I)	$(MeO_2C)_2C:C(CO_2Me)_2$	(II)	Ratios
Z = Br[a] ..	68·7	15·1	6·66	1·00:0·219:0·097
I[a] ..	74·3	12·9	7·43	1·00:0·174:0·100
Br[b] ..	22·0	1·88	2·08	1·00:0·085:0·095
I[b] ..	19·9	2·02	1·79	1·00:0·101:0·090
Br[c] ..	71·6	22·9	5·72	1·00:0·320:0·080
I[c] ..	78·8	15·0	5·92	1·00:0·191:0·075
No Catalyst[c] ..	9·45	1·82	0·00	1:00:0·192

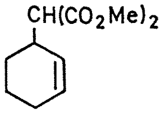
[a] Commercial cyclohexene.
[b] Commercial cyclohexene filtered through alumina.
[c] Commercial cyclohexene filtered through alumina, then 0·07 mmole benzoyl peroxide added.

All reactions were run as follows: A solution of 0·02 mole of dimethyl diazomalonate in 0·25 mole of cyclohexene was added at the rate of 6 drops per min to 0·25 mole of refluxing olefin containing the catalyst or catalyst plus peroxide. After 24 h at reflux, the excess of olefin was removed by distillation, and the residue analysed by g.l.c. using diglyme as an internal standard.

catalyst activity. This is nicely supported by comparable experiments carried out with the addition of benzoyl peroxide (see Table) or Vazo.‡ Equally surprising is the fact that if the catalyst is treated with benzoyl peroxide in benzene prior to the addition of olefin or diazo-compound a catalyst far superior to any previously observed is obtained. It therefore seems extremely unlikely that the catalytic decomposition of diazo-compound is proceeding in a radical manner initiated by peroxides and that triplet carbenoid is therefore not an artifact. The inescapable conclusion is that the hydrocarbon and/or benzoyl radicals react with the catalyst to generate new catalysts which are superior to the material added. We are currently investigating the structure of the active catalyst species.



(I)



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‡ E. I. du Pont de Nemours and Company, trademark for azo-bis-isobutyronitrile.

[1] D. S. Wulfman, F. C. Carman, B. G. McGiboney, E. K. Stefien, and B. W. Peace, *Preprints, Division of Petroleum Chemistry, Amer. Chem. Soc.*, 1971, **16** (**1**), B81.

[2] W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.

[3] To be published elsewhere.

[4] D. S. Wulfman, B. W. Peace, and E. K. Steffen, *Chem. Comm.*, 1971, in the press.