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COPPER SALT CATALYSED REACTIONS OF t-BUTYL PERBENZOATE WITH *CIS*- AND *TRANS*-*p*-MENTH-2-ENE

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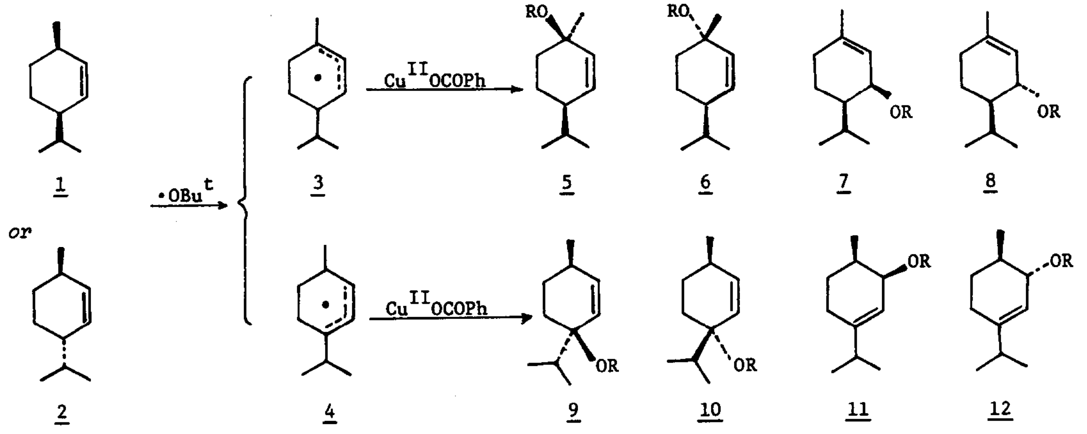
Previous extensive investigations of the copper salt catalysed reactions of olefins with peresters have been mainly confined to acyclic substrates.[1] In the expectation that reactions of substituted cyclic olefins would reveal new details of mechanism we have now analysed the mixtures of products formed by treatment of *cis*- and *trans*-*p*-menth-2-ene, 1 and 2, with t-butyl perbenzoate in benzene in the presence of small amounts of either cupric octanoate or tris-bipyridyl cupric octanoate. Each substrate afforded a mixture of eight allylic benzoates (5a-12a) which was reduced with lithium aluminium hydride and analysed by g.l.c. (20' x 1/8", 0.75% FFAP; T = 105°) using as reference authentic alcohols (5b-12b) synthesized by unambiguous routes.†



Scheme

a; R = COPh b; R = OH

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† Satisfactory analytical and spectral data have been obtained for all new compounds.

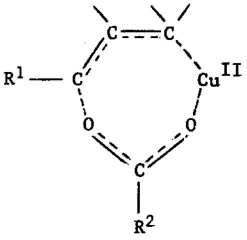
The products formed are those expected on the basis of the accepted mechanism[1] (Scheme) involving the intermediacy of allylic radicals which are converted into esters by interaction with Cu^{II} carboxylate. However, our data (Table) clearly show that the distribution of products is dependent upon the co-ordination state of the copper catalyst. Those compounds 5a, 6a, 9a, 10a which contain a disubstituted double bond comprise the major proportion of the total products from reactions catalysed by cupric octanoate, whereas the complex copper salt affords relatively higher combined yields of the trisubstituted olefins 7a, 8a, 11a, and 12a. A similar dependency of the relative yields of positional isomers of allylic esters formed from acyclic olefins on the nature of the copper salt catalyst has been previously noted.[2,3]

Copper Salt Catalysed Reaction of cis- *and* trans-p-*menth-2-ene with t-Butyl Perbenzoate*

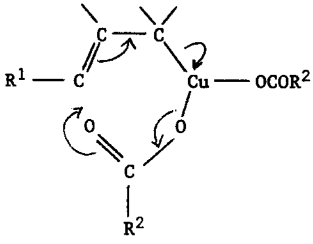
Olefin	Catalyst[a]	Yields of Products[b]								Total Yield
		5	6	7	8	9	10	11	12	
1	Cu.oct	8.8	36.1	0.7	4.1	7.0	26.9	3.4	13.0	77
2	Cu.oct	10.0	49.1	0.6	4.9	5.8	23.2	0.9	5.5	89
1	Cu.bp.oct	14.1	15.3	4.0	4.9	2.0	6.0	14.1	39.6	32[c]
2	Cu.bp.oct	19.8	21.0	4.6	7.7	2.2	7.9	10.2	26.6	12[d]

[a] Cu.oct = cupric octanoate, Cu.bp.oct = tris-bipyridyl cupric octanoate; [b] mols per 100 mols of total identified products; [c] three unidentified products (c. 3%); [d] four unidentified products (c. 1%).

The cupric octanoate catalysed reaction is highly stereo-selective and yields a large preponderance of those products 6a, 8a 10a, 12a formed by introduction of a benzoate group *anti*- to an alkyl substituent. The cupric-bipyridyl complex shows similar but reduced stereo-selectivity in its reaction with the allylic radical 4, but its reaction with the allylic radical 3 shows no stereo-selectivity and in this respect is similar to autoxidation of *p*-menth-1-ene, a process which also involves the intermediacy of 3.[4]



13



14

Of the various mechanisms proposed for the reaction of allylic radicals with cupric carboxylate[2,3,5,6] those that best accommodate the results reported here involve ligand transfer either in a one-step process through the cyclic transition state 13[2] or in two steps *via* formation of the organo-copper intermediate 14[6] which undergoes intramolecular allylic substitution through a transition state similar to 13. We favour the latter hypothesis because of its close resemblance to the accepted mechanism for the formation of olefins from alkyl radicals by cupric carboxylate,[6,7] and because it best accounts for the observed regio- and stereo- selectivity. The formation of organo-copper intermediates from the radicals 3 and 4 would be expected to involve bonding of the copper to the less hindered secondary carbon centres in a *trans*-relation to the adjacent alkyl substituents. Intramolecular allylic substitution in such intermediates would lead to the two major products 6a and 10a. The observed reduction in regio-and stereo- selectivity and in the yields of unrearranged benzoates when tris-bipyridyl cupric octanoate is used as catalyst is thought to be associated with a decreased ability of the complex to form organo-copper intermediates. The reaction probably then proceeds, at least in part, *via* the allylic carbonium ions formed from the radicals 3 and 4 by electron transfer.[3,5] In accord with this hypothesis the reaction in the presence of the cupric bipyridyl complex afforded unidentified products believed to arise by skeletal rearrangements.

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