

THE SIMULTANEITY OF ALLENE CYCLOADDITIONS. THE  
REACTION OF TETRACYANOETHYLENEOXIDE WITH ALLENE.<sup>1</sup>

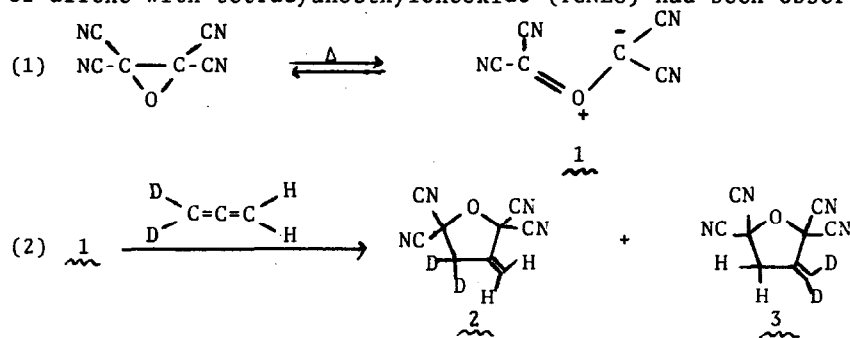
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In our earlier communications dealing with the simultaneity of (2+2) and (2+4) cycloadditions of allene, it has been concluded that intramolecular isotope effects with values  $k_H/k_D > 1.00$  derive from a non-concerted, probable diradical process, and that when  $k_H/k_D < 1.00$  a concerted mechanism is likely.<sup>3,4</sup>

Table I. Isotope Effects for Allene Cycloadditions

Type Process	Reagent	$k_H/k_D$	Ref.
(2+2)	Allene	1.14 ± .02	4
(2+2)	Acrylonitrile	1.21 ± .02	3
(2+2)	1,1-difluoro-2,2-dichloroethylene	1.15 ± .04	5
(2+4)	Hexachlorocyclopentadiene	0.90 ± .03	3

We wish now to report the results of an investigation of a (2+3) cycloaddition involving allene which is consistent with this pattern. The reaction of allene with tetracyanoethyleneoxide (TCNEO) had been observed earlier,<sup>6</sup> and



we find that yields can be obtained as high as 75% using excess allene at low conversion. The reactions are carried out in dioxane, using 1,1-dideuterioallene, under vacuum in sealed tubes at 130° for ten hours and an isotope effect of  $k_H/k_D = 0.93 \pm 0.01$  (.97 perdeuterium) can be obtained directly from nmr ratios of the vinylic to allylic protons in the glpc purified product. These results are consistent with those obtained by Bayne and Snyder in their study of TCNEO with isotopically labelled styrenes, where they observed  $(k_H/k_D)_\alpha = 0.96$  and  $(k_H/k_D)_\beta = 0.97$ . The results are best explained by a concerted process being involved for step 2 in the reaction and are inconsistent with rate-determining formation of a diradical or dipolar intermediate. With regard to Firestone's hypothesis of rate-determining destruction of a dipolar intermediate, it seems to us that whether such destruction is rate-determining or relatively fast should have little or no bearing on the observed secondary deuterium isotope effects of the process. Thus, since we have shown that fast destruction of apparent diradical intermediates leads to intramolecular  $k_H/k_D > 1$ ,<sup>3,4</sup> there seems to be no apparent reason to expect  $k_H/k_D$  to be  $< 1$  for Firestone's mechanism.

#### References

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